Competitive sorption studies with nylon 6 and active carbon.

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COMPETITIVE SORPTION STUDIES WITH NYLON 6 AND ACTIVE CARBON

THESIS

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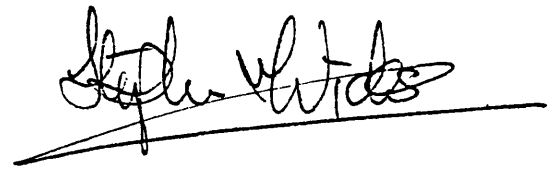
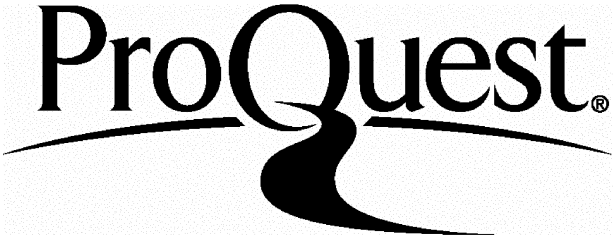
This research has been carried out in the School of Pharmacy and Pharmacology, under the supervision of N.E. Richardson, B Pharm., PhD., M.P.S and B.J. Meakin, B.Pharm., F.P.S.





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CONTENTS

SUMMARY

This work involves a fundamental investigation of the effect of competitive sorption processes on the equilibrium and kinetics of sorption by two sorbent materials, active carbon granules and nylon 6 powder, using simple aromatic model solutes. In addition the influence on these processes of coating the active charcoal granules with a thin layer of nylon 6 was also studied. The Thesis is divided into three parts, the Introduction, Experimental and Discussion Sections. The Introduction deals with the properties of active carbon and nylon 6. This is then followed by a discussion of the sorption, diffusion and permeability processes in sorbent materials, and the physicochemical factors that influence them. The Introduction is concluded with a section on competitive sorption phenomena.

The Experimental section describes the physical characterisation of the sorbent materials. This is followed by details of the determination of the sorption isotherms for the interaction of the model solutes from both single and binary solute solutions with the sorbents. The phenolic compounds were found to have a high affinity for nylon 6 compared to the benzoic derivatives and binary solute mixtures of these phenolic compounds showed competitive sorption phenomena which was accompanied by a co-plasticisation effect at higher concentration. The benzoic acid derivatives showed no competitive effects but a temperature transition effect on sorption was found for these compounds which was absent for the phenolic compounds. Sorption of the model solutes by active carbon from binary solute solution showed evidence that a competitive interaction was occurring, the extent of the competition being related to the

concentration of the competing species. The application of a thin coat of nylon 6 to the charcoal granules did not result in a significant change in the sorption isotherm type found although the sorption capacity was lowered. The final section of the experimental work deals with the kinetics of sorption of the sorbents, again from both single and binary solute solutions. The presence of the coat and other competing species present in solution were both seen to influence the kinetics of sorption.

The final section of the thesis deals with the discussion of the experimental results obtained. The main conclusion drawn is that the interaction of the model solutes with the active carbon and nylon 6 may be accounted for by the concept of the conservation of diffusing mass thus allowing them to be directly compared despite marked differences in their physical nature and sorption characteristics. The mechanisms of competitive sorption are also discussed and compared with models proposed in the literature. The sorption characteristics of the composite sorbent are accounted for in terms of the interaction characteristics of its two components to assess whether selectively permeable film coats could be used to improve the sorption efficiency of active carbon in multi-solute systems.

SECTION 1

INTRODUCTION

1 1 THE USE OF SORBENTS IN PHARMACY AND MEDICINE

Two types of sorbent materials are widely used in Pharmacy and Medicine. Inorganic adsorbents such as kaolin, magnesium trisilicate and active carbon can remove toxic solutes from solution or biological fluids when taken in the form of fine powders.

Synthetic plastic materials also possess sorbent properties which has led to their development as dialysis membranes or as components of sustained release drug delivery devices.

1.1.1 Inorganic Sorbents

Sorbent materials for gastrointestinal detoxification should ideally have a broad spectrum of affinity and capacity for common toxic and poisonous substances and be able to complex with them in the presence of other solutes found in gut fluids. Kaolin, magnesium trisilicate and active carbon fulfil these criteria to varying extents and are, clinically, the most widely used medicinal sorbents. Magnesium trisilicate is the least efficient of these adsorbents and also possesses weak antacid properties. This sorbent forms a gel on contact with the acidic stomach contents and has been shown to interact with tetracyclines, anticholinergics and other therapeutic agents, reducing their absorption from the gut (Swinyard 1975). Kaolin is widely used in aqueous suspension for the treatment of diarrhoea arising from ingestion of irritant materials. Kaolin, a hydrated aluminium silicate, structurally comprises of flat platelets with negative charges present on the flat faces and positive charges at the edges (Martindale 27th Edition).

It has a broad spectrum of activity with respect to basic drug molecules which associate by the formation of a charge transfer

complex but the affinity for acidic drugs is low (Armstrong and Clarke 1976, Crammer and Davies 1972). The effectiveness of kaolin is further limited by the pH sensivity of the charge transfer complex which is highly stable at pH 9.0 but unstable at low pH values.

Active carbon is widely used in gastrointestinal detoxification and its remarkable sorption properties are exploited in a wide range of other Pharmaceutical and Medicinal applications. The use of active carbon, as a general panacea, has been known since the time of the Egyptian dynasties where its application in the treatment of a wide range of diseases was first recorded on a papyrus dated circa 1550 BC. Active carbon detoxification treatment was referred to by Hippocrates (400 BC) and Pliny (50 AD) for such diverse ailments as epilepsy, vertigo and anthrax (Cooney 1980). The broad adsorption spectrum and high adsorptive capacity of active carbon is exploited in modern medicine in the treatment of poisoning. Interactions with virtually all known potential toxins has led to it being regarded as a "universal antidote" (Boehm and Oppenheim 1977). Active carbon has been shown to adsorb a wide range of household and environmental poisons including alkaloids, salicylates, paracetamol and barbiturates (Decker et al, 1968; Chin et al, 1970; Lipscombe and Widdop, 1975).

The slow mass transfer rate associated with sorption from solution by active carbon or the reverse desorption process has resulted in its use for sustaining the release of drug solutes acting locally in or on the gut. Active carbon has successfully sustained the release of eserine for the treatment of atonia of the intestinal wall muscle and hydroxyaminophenylarsonic acid for the treatment of bowel infestation and infection (Cooney 1980).

A technique, utilising the high adsorptive capacity of active

carbon, has been developed for the treatment of systemic toxaemia arising from drug overdose or renal or hepatic failure. This technique, referred to as haemoperfusion, involves passing the patient's blood through a column of active carbon granules via an extracorporeal shunt (Yatzidis 1964). The active carbon granules are generally coated with a thin layer of a polymer, such as a hydrogel, to increase their biocompatability (Hagstamm et al 1966).

Clinical haemoperfusion is already widely used in poisons units within the U.K. and its use in chronic renal and hepatic failure has also been suggested either as an adjunct or alternative to conventional haemodialysis (Giordano 1980).

Recent advances in carbon technology have led to the development of active carbons that retain the morphological characteristics of the materials from which they are prepared. For example, active carbon has been manufactured in the form of a flexible woven cloth (Bailey 1973) which has found use as a component of dressings for malodorous wounds (Butcher 1976). Active carbon in the form of uniformly sized active carbon spheres has also been developed as a stationary phase packing material in the gas chromatographic analysis of cyclopropane, an anaesthetic (Analabs 1980). The application of these two materials as components of haemoperfusion systems has also been studied; they were found to have much greater mass transfer rates than conventional granular active carbons (Gaylor et al 1976, Amano 1978).

1.1.2 Synthetic Sorbents.

A wide range of synthetic polymers have been developed, since the Second World War, which have been used for Pharmaceutical and Medical purposes. Such materials include polyethylene,

polypropylene, polyvinylchloride (P.V.C) and nylon. Certain polymeric materials are capable of absorbing solutes from solutions brought into contact with them and so may be classified as sorbents. Apart from their use in packaging, these materials have been studied extensively as components of sustained release dosage forms, gastrointestinal detoxifying agents, chromatographic stationary phase materials, and for a wide range of Pharmaceutical and Medical applications.

1.1.2.1. Sustained Release Dosage Forms

Sustained release dosage forms, based on plastics materials, fall into two major categories. Firstly, the reservoir device where a concentrated reservoir of drug is contained within a rate controlling polymeric membrane and secondly, the matrix device where drug dispersed within the polymeric matrix, is released by a leaching type process. The reservoir devices, developed for use as sustained release dosage forms, are of two main types. The first type is used as a non-erodible depot preparation and is of a size which can contain a relatively large amount of drug and will remain at the site of insertion.

Ethylenevinylacetate copolymers have been used as components of two commercial reservoir devices. The Ocusert is used to sustain the release of pilocarpine into the eye and the Progestasert sustains the release of progesterone locally in the uterus (Baker and Lonsdale 1975, Roseman 1979). A novel oral reservoir dosage form has also been developed based on this principle. The Oros device consists of a concentrated drug reservoir encapsulated within a membrane which is selectively permeable to water, in which a small aperture has been

drilled using a laser.

Water flows into the device, at a rate controlled by the membrane and dissolves the drug, increasing the internal pressure. The concentrated drug is then forced out of the aperture at a rate which is indirectly controlled by the selectively permeable membrane (Theeuwes 1976).

The second type of reservoir dosage form consists of small, polymeric drug containing particles, called microcapsules, which can control the release of the drugs. The controlled release of pentobarbitone has been achieved using nylon microcapsules (Luzzi et al 1970) and sulphadiazine by gelatin microcapsules (Nixen and Walker 1971).

The Gradumet tablet is an example of a polymeric dosage form in which the drug is dispersed throughout the matrix as opposed to being present in an isolated reservoir. The Gradumet consists of a highly porous non-erodible plastic matrix containing a filler material mixed with the drug. The filler is hydrophilic and attracts water resulting in dissolution of the drug, which is then released at a controlled rate by a process of intrapore diffusion (Roseman 1979).

Plastics materials such as polyethylene, polypropylene and nylons have been investigated for their use as insoluble tablet matrices. Vora (1964), for example, has reported on the use of P.V.C. as a tablet matrix for sustained release preparations of aspirin.

1.1.2.2 Detoxification.

Whilst Cellophane has been used for many years as the standard membrane in kidney machines, other polymers, including nylons, are now being investigated for their applicability in dialysis

(Kostenbauder 1969). A recent study has reported on the development of a sorbent membrane consisting of active carbon bonded to cellulose with a second layer of thin cuprophan serving as the biocompatable element in contact with blood (Gurland et al 1978).

Polymeric sorbents are also used for detoxification in poisoning incidents or toxaemia. Cholestyramine, an ion exchange resin, is administered orally to effect the removal of weakly acidic toxins. Therapeutic agents such as aspirin, warfarin and phenylbutazone are also efficiently adsorbed by cholestyramine (Boehm and Oppenheim 1977) and its use has been recommended in the clinical adsorption of paracetamol (Dordoni et al 1973).

1.1.2.3 Chromatography.

Nylon 6 is presently used as a stationary phase material for the thin layer chromatographic analysis of solutes which can form strong hydrogen bonds with the amide group in the matrix (Bark and Graham 1967). These include aromatic solutes possessing the phenolic,hydroxyl and nitro groups.

1.1.2.4 Containers and Packages.

Polymeric materials are widely used in Pharmacy as containers and packages due to their lightness, toughness and resistance to chemical attack. Plastics materials have been shown to interact with the components of liquid formulations resulting in the loss of active materials and excipients, or allowing the ingress of atmospheric gases all of which affect the stability of the formulation. (Richardson 1973, Autian et al 1958). The sorption of a particular molecular species by the polymer is generally instrumental in effecting the spoilage of liquid formulations (Richardson 1973, Autian 1963).

1.2 THE ORIGIN AND SCOPE OF THIS WORK.

Sorbent materials used for Pharmaceutical and Medical purposes will usually encounter complex multisolute solutions.

Gastrointestinal adsorbents come into contact with gut fluids and Pharmaceutical formulations, contained within polymeric materials, may be composed of more than one adsorbate solute.

Sorbent materials are evaluated on the basis of fundamental sorption studies which attempt to establish and characterise their interaction with specific solutes. Generally, these studies have only involved the adsorption of a single solute from simple solution.

Such single solute adsorption studies can provide much useful information about the nature and mechanism of the interaction but are limited in evaluating the performance of the sorbent in more complex media. This has been shown by Goldenhersh (1976) and Tsuchiya and Levy (1972) who found that the sorption of various toxins by active carbon was lowered in the presence of endogenous compounds found in biological fluids. Sparks (1975) has suggested that single solute sorption studies may, therefore, overestimate the affinity and capacity of the sorbent for a specific solute in the presence of competing endogenous species.

Preliminary studies, in the biomedical field, into the inhibition of sorption due to multisolute uptake have investigated the sorption of specific solutes from biological media (Goldenhersh 1976).

Other work has been concerned with the sorption of solute from simple solutions using coated and uncoated adsorbents which are, structurally, clearly unrelated. (Skalsky & Farrell 1979). In addition, several workers in the chemical engineering and allied fields have investigated competitive sorption on to active carbon; such

such reports have been primarily concerned with the theory relevant to the prediction of multisolute sorption equilibria from single solute data (Radke and Prausnitz 1972b, Weber and Morris 1964). Although the overall inhibitory effect of competitive sorption from multisolute solutions has been clearly demonstrated, the fundamental mechanisms associated with the process are still not fully understood. It was, therefore, decided to initiate a fundamental study of adsorption from binary solute solutions using simple model systems.

1.2.1 Selection of the Model Systems.

Two sorbent materials were selected for this investigation, nylon 6 and active carbon. Nylon 6 was chosen as the characteristics and factors affecting the sorption of weak electrolytes from single solute solutions have been extensively studied previously in these laboratories (Richardson 1973, Ho, 1977). Nylon 6 is readily obtained in an almost pure form (Richardson 1973) in the absence of additives such as plasticizers which have been shown to modify the sorption of solutes by plastics (Bray 1977). The second adsorbent studied was active carbon, an example of a material that is also widely used in Pharmacy and Medicine. Active carbon was used in a granular form that had been specially purified to remove trace metals and contaminants to produce a medicinal grade product suitable for use in haemoperfusion columns (Fennimore, Personal Communication Simmonite, 1973).

The model solutes selected were either phenolic in nature (phenol and 4-nitrophenol) or simple benzoic acid) which possess functional groups common to many drugs and preservatives.

When used in haemoperfusion columns, active carbon granules are coated with a thin layer of polymer which performs several functions.

The polymer coat decreases the incidence of thrombus formation, thus promoting the biocompatibility of the surface of the carbon, by preventing the shedding of fine particles. The polymer coat may also confer some degree of selectivity on the adsorbent by differentially controlling the nature of materials allowed access to the adsorption sites within the carbon pores. Sparks (1975) has suggested that the sorption capacity of the sorbent for a specific molecule may be increased by the use of a selective polymeric microcapsule wall around the granule. Meier et al (1972) have reported that cellulosic coatings confers selectivity for certain solute species by a "like-dissolving-like" principle e.g. hydrophobic molecules diffusing more rapidly through hydrophobic coatings. Huang (1974) has reported on the use of charged polymer films which specifically select species of opposite charge.

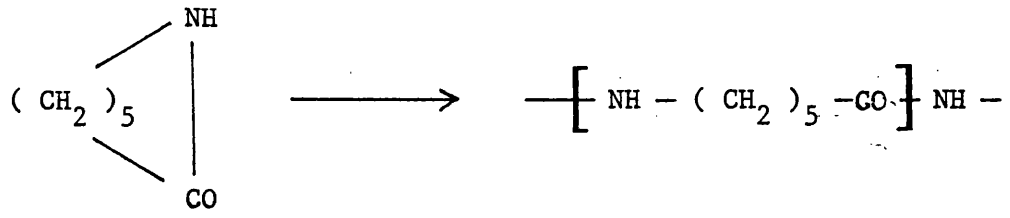
The sorption studies carried out in this work were, therefore, extended to include an investigation of the interaction of the model solutes with active carbon granules that had been coated with a thin film of nylon 6.

1 3. MATERIALS.

1 3.1 Nylon 6.

Nylon is the generic name for a series of polymers also known as polyamides. Nylon 6 is a linear homopolymer and shows the typical structure of the polyamide group consisting of a long chain of methylene groups which are interrupted by an amide group after each fifth CH_2 group. The polymer thus has both polar and non-polar characteristics conferred by the amide and methylene groups respectively Nylon 6 is synthesized from caprolactam by scission of the lactam ring. about 90% of the monomer being converted to the

polymer. (Encyclopedia of Polymer Science & Technology).



The polymer matrix is heterogeneous in nature consisting of both amorphous and crystalline regions. Both inter and intrachain hydrogen bonds exist between the amide groups. When the polymer chains are aligned closely to each other, as shown schematically in figure 1.1, the extent of interchain hydrogen bonding is at a maximum resulting in a highly stable crystalline configuration.

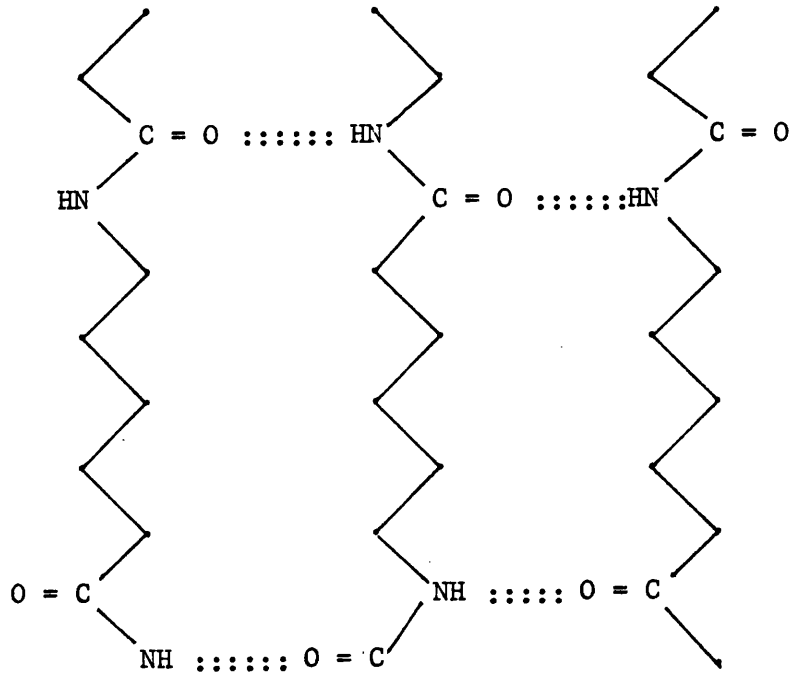


Figure 1.1 Schematic Representation of Hydrogen Bond Formation Between Nylon 6 Molecules.

The amorphous regions, however, are much less extensively hydrogen bonded. The presence of crystalline regions results in the polymer having a high melting point and impact strength. The proximity of the amide chains and thus the extent of bond formation is influenced by environmental factors such as physical stress (Brysdon 1970), hydration (Autian 1963) and temperature (Lord 1974). Lord (1974) showed that the polymer chains could align in the same or opposite directions with respect to one another which are referred to as the parallel and anti-parallel configurations, respectively. If the matrix is heated to 40^{o} - 50^{o} the methylene sequences in the crystalline regions with parallel configuration acquire sufficient mobility to twist, enabling the extent of hydrogen bonding to be enhanced. The resulting bond formation cannot attain any degree of perfection, however, because of the structural constraints of the anti-parallel regions which physically restrict excessive movement in the parallel region. Further heating in the range of 150^{o} causes twisting and consolidation of bonding in the anti-parallel region. This occurs with a consequent disruption of hydrogen bonding in the parallel region previously established at the low temperature (Lord 1974).

Hydration of the matrix by specific bond formation between water molecules and unassociated amide groups has been established using vapour phase adsorption techniques (Puffr and Sebenda 1967). Water can gain access to the matrix via the amorphous regions but cannot penetrate the relatively denser crystalline regions. Three types of water-amide group bond have been postulated which are shown schematically in figure 1.2.

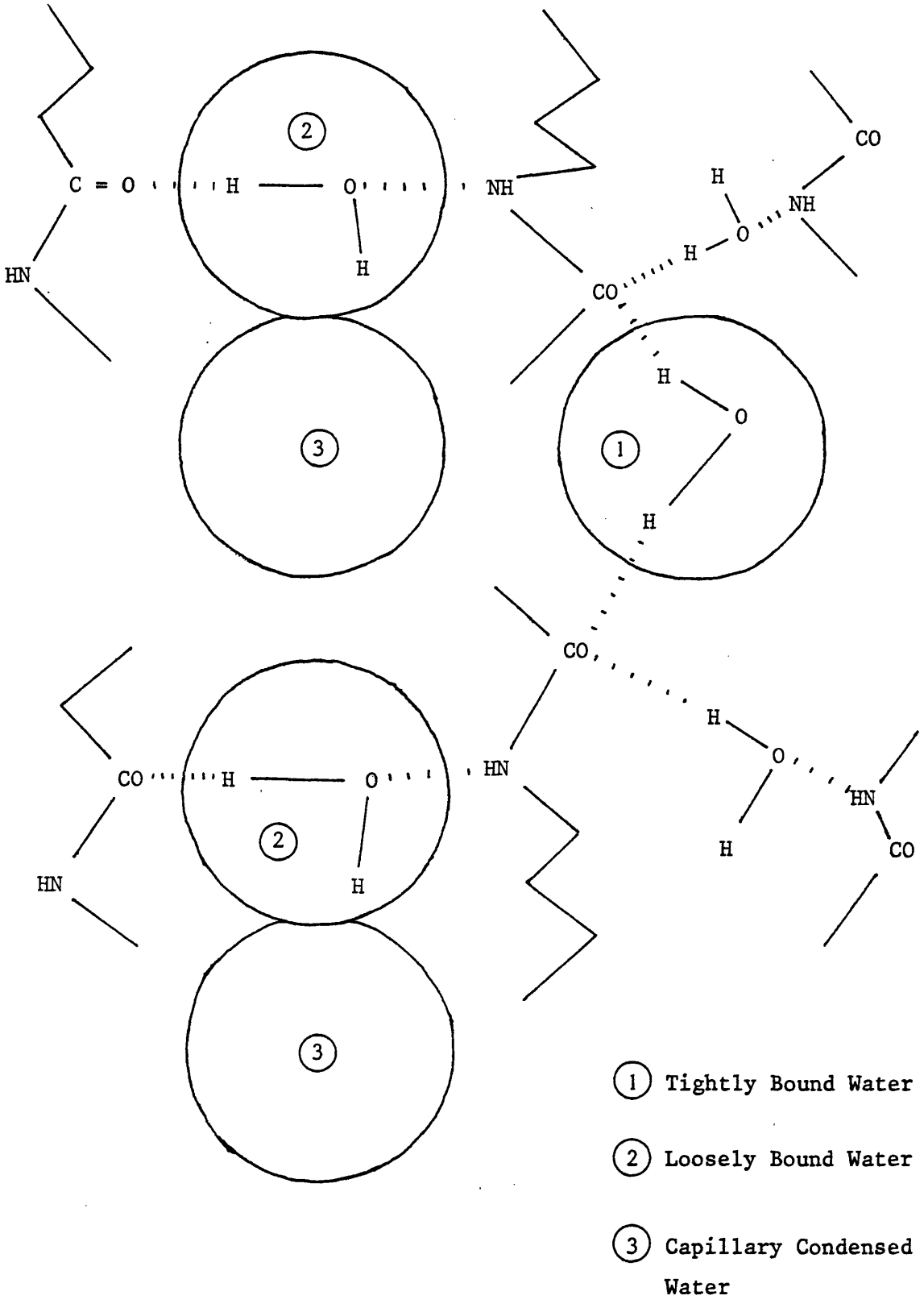


Figure 1.2 Model for the Distribution of Sorbed Water in Nylon 6 (Puffr and Sebenda 1967).

The water molecules referred to by the numbers 1, 2 and 3 in figure 1.2 correspond to tightly bound, loosely bound and capillary condensed water respectively. Tightly bound water molecules form a double hydrogen bond between the carbonyl free-electron pairs of two adjacent amide groups. The loosely bound water molecules are more numerous and can bind by joining existing hydrogen bonds between the carbonyl and amide groups of adjacent amide links. Capillary condensation occurs by the self association of incoming water molecules with existingly bound water, with the condensed water retaining a similar activity to that of bulk phase water. In summary, therefore, the nylon 6 matrix is held together by interchain hydrogen bonds to maintain a partially crystalline, partially amorphous structure. Chemically the matrix consists of polar regions and nonpolar regions due to the presence of the amide and methylene groups in the polymer chain. The entire matrix is a dynamic structure capable of modification under the influence of external physicochemical factors. The amorphous areas are accessible to water which is capable of hydrating unassociated amide groups by specific hydrogen bond formation. The synthesis, structure and properties of other common polyamides have been discussed in detail elsewhere. (Richardson 1973, Ho 1977).

1.3.2. Active Carbon

The various forms of carbon are summarised in figure 1.3

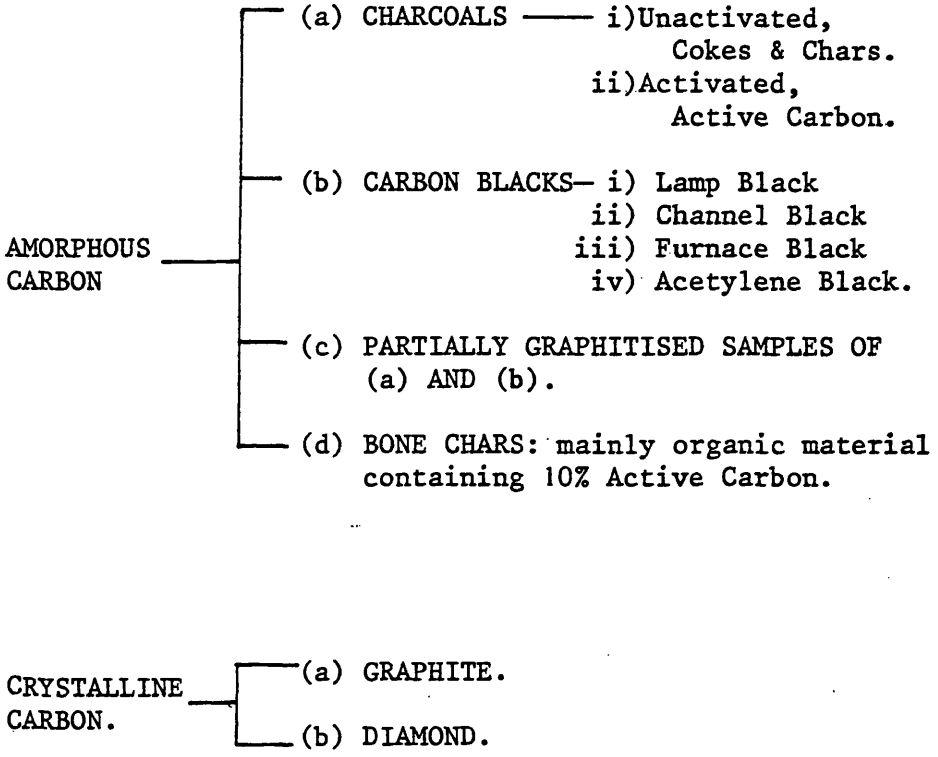
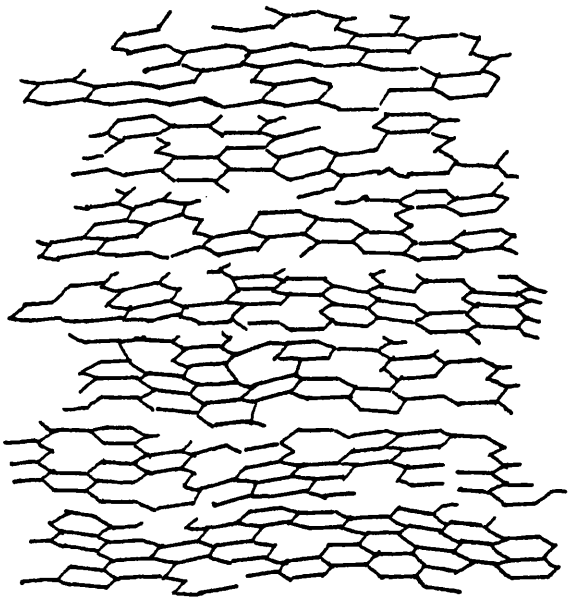


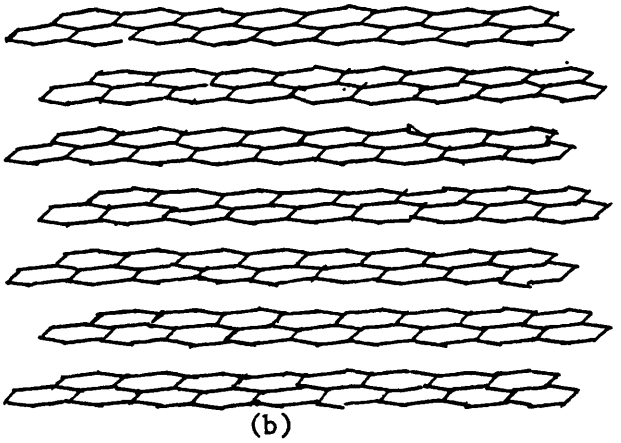
Figure 1.3 Allotropes and Subclasses of Carbon

This study is concerned with the active carbon subclass of the amorphous allotropic form of carbon. The aim of a manufacturing process producing active carbon is to convert a hydrocarbon precursor material into pure carbon, and develop an extensive porous network within the resultant material. The processed material, usually cellulosic in nature, is initially burnt at relatively low temperatures to remove most of the non-carbon elements which are given off as volatile products of chemically diverse pyrolytic reactions. If this process is carried out in the absence of air it is referred to as coking and the end result is a low activity coke which possesses

a rudimentary internal pore structure. To obtain active carbon, the pore structure of the coke is consolidated by oxidation, where the pore system is extended and oxide groups are produced on the pore walls by chemical reactions at the surface. Air, chlorine, oxygen and sulphur vapours may all be used as oxidants, but steam is generally preferred on an industrial scale as the resulting activation reaction is endothermic and thus more easily controlled. Activation via the coke intermediate is carried out, industrially, by a two stage process. The same result may be achieved by simultaneous coking and activation. This method is termed "chemical activation" and involves saturation of the cellulosic precursor with inorganic oxidising or dehydrating agents i.e. zinc chloride, phosphoric acid or potassium sulphide, followed by anoxic pyrolysis. The precursor is burnt to form a coke, and at the higher temperatures used the inorganic salts liberate oxidising gases, in situ thus instantaneously activating the coke at it forms. The convenience of this single unit process method of production is usually offset by the need to remove the high inorganic ash residues by washing. The resulting active carbon consists of a mass of elemental carbon containing a tortuous highly complex pore system The mass of elemental carbon consists mainly of atoms present in a turbostratic arrangement (figure 1 4a). The atomic arrangement within the elemental mass is, however, heterogeneous and certain microcrystallites of a graphitic structure (figure 1 4b) are also present a few layers in thickness and less than 100Å in width (Mattson and Mark 1971).



(a)



(b)

Figure 1.4 Schematic Diagram Comparing (a) a Turbostratic Arrangement of Carbon Atoms with (b) a Graphitic Structure

The level of structural imperfections in active carbon is very high which results in a diverse variety of edge carbon oxidation reactions during activation. Seven examples of the surface oxide groups that have been proposed are summarised in figure 1.5 (Mattson and Mark 1971).

Active carbons owe their high sorption affinity and capacity to their complex internal pore network. The pore network consists of a series of different sized pores which have been classified by Dubinin (1955) as macro, meso and micropores. The larger macro and mesopores, with pore radii between 1200Å to 160,000Å, have been characterised using mercury porosimeter techniques (Ritter and Drake 1947). The smaller micropores have radii reported to be as low as 10Å (Kipling 1956), and are usually investigated by B.E.T. gas adsorption techniques (Cohan 1938). The high activity of porous carbon has been shown to be due almost entirely to the abundance of micropores (Juhola and Wiig 1949). These workers determined the B.E.T. surface area in the various porous regions of a Darco G active carbon and showed that the macropores and mesopores accounted for only 3 $m^2 g^{-1}$ out of a total surface area of 1500 $m^2 g^{-1}$, the remaining excess area existing in the micropore network (Juhola and Wiig 1949).

1.4 CLASSIFICATION OF THE TERMS USED IN DRUGS-SORBENT INTERACTIONS

The various types of solute-sorbent interactions that may occur when an adsorbent is placed in contact with a solution of a specific solute are summarised in figure 1.6.

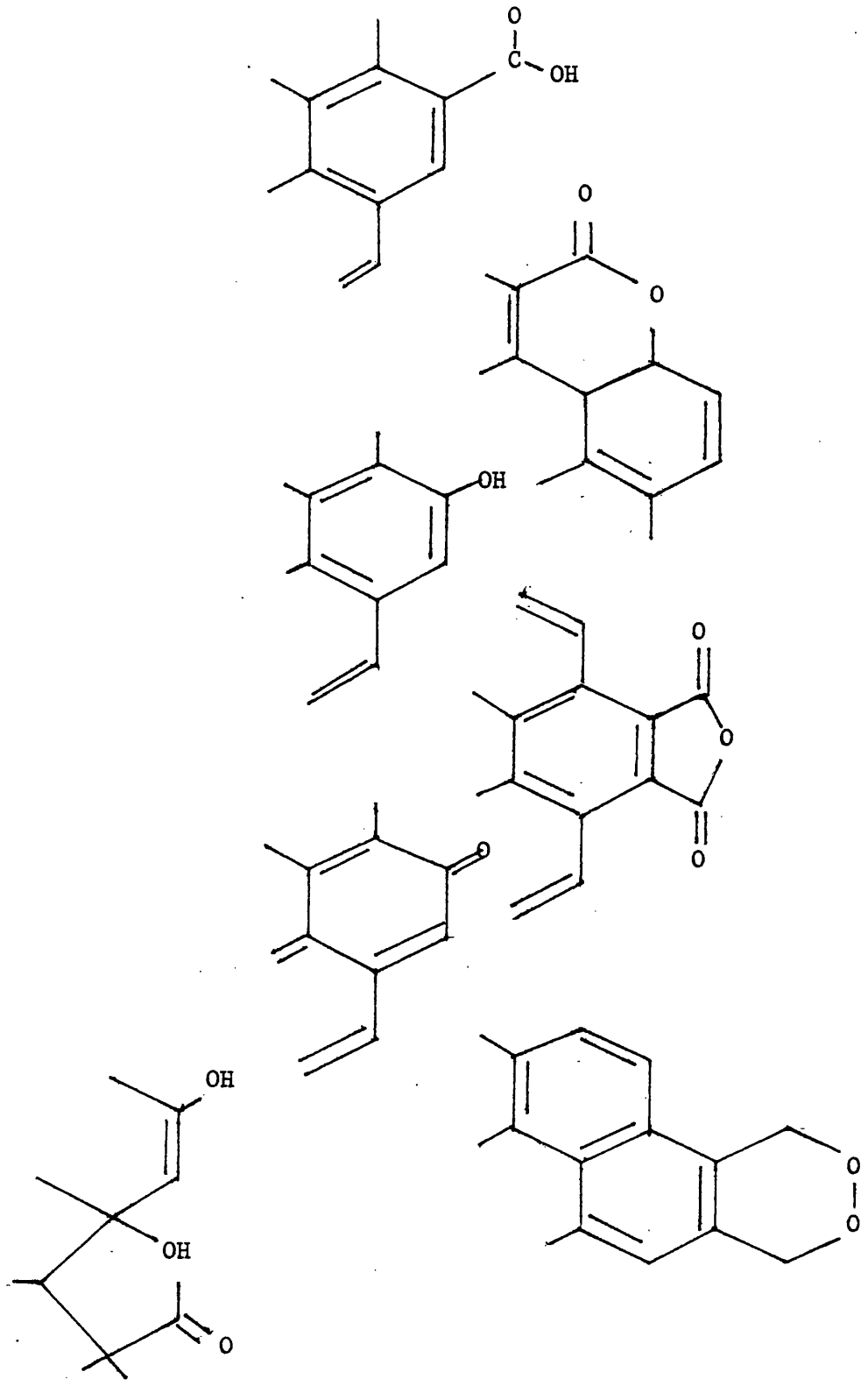


Figure 1.5 Surface Oxide Complexes Present on the Surface of Active Carbon Determined by Spectroscopic Analysis.

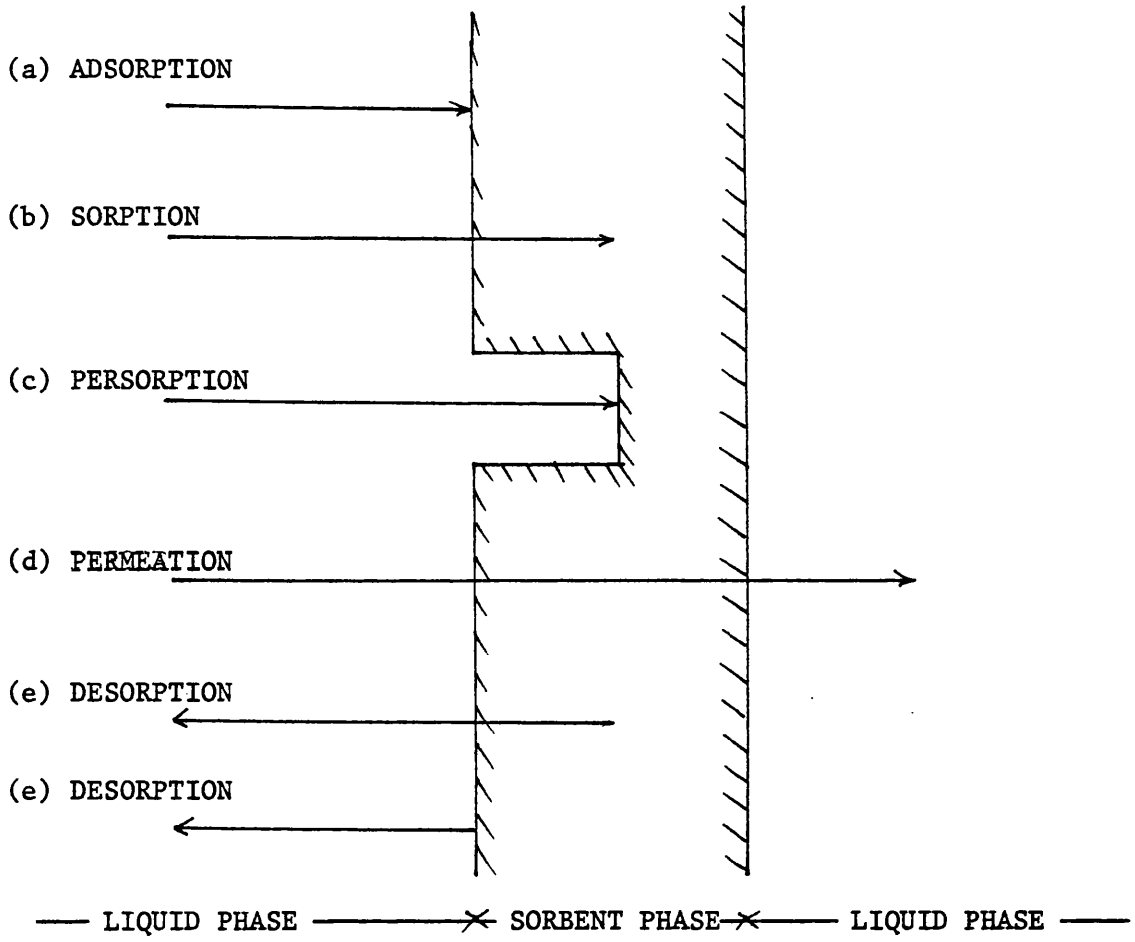


Figure 1.6 Interaction Processes in Sorbent Materials.

a) Adsorption involves the concentration of a component of the sorption system at an interface between phases. In this study the interaction takes place at the solid-liquid interface. The adsorbate molecules are momentarily immobilised at the interface during the adsorption process such that when the rate at which molecules arrive equals the rate at which they depart, the system is said to be in a state of dynamic equilibrium. In this study the term adsorption is applied to the net transfer of solute from bulk solution to the interface as opposed to its frequent use to describe the momentary immobilisation of a single solute molecule at the interface.

b) Sorption is a term applied to an interaction whereby the solute can penetrate into the bulk of the adsorbent by crossing an interface. The term, therefore, describes both the adsorption stage at the surface and the penetration stage. Sorption processes are typically shown in solute-polymer sorption systems (Richardson 1973).

c) Persorption describes the process whereby solute molecules penetrate a series of pores in the bulk of the sorbent rather than at the molecular level, as is the case in sorption (Adamson 1967). This process is found in the interaction of solutes with porous adsorbents such as active carbon.

In the literature, and in this work, the term sorption is applied to the uptake of solutes by sorbents when the specific mechanism is unclear in addition to the particular meaning given above.

d) Permeation arises when a transport system is created in which solute molecules cross a barrier which separates a solute solution from a second bulk phase. The mechanism of permeation takes place primarily by the sorption, distribution and diffusion processes illustrated schematically in figure 1.7. Solute initially adsorbs on to the surface of the sorbent membrance from the donor compartment (1) and diffuses through the structure by a sorption process (2 - 5). After a given time interval a concentration gradient exists across the entire membrane thickness at which point solute desorbs into the receptor compartment (6). The transfer of mass continues under the influence of the now decreasing concentration gradient in the polymer (7) until equilibrium in all three phases is attained (8).

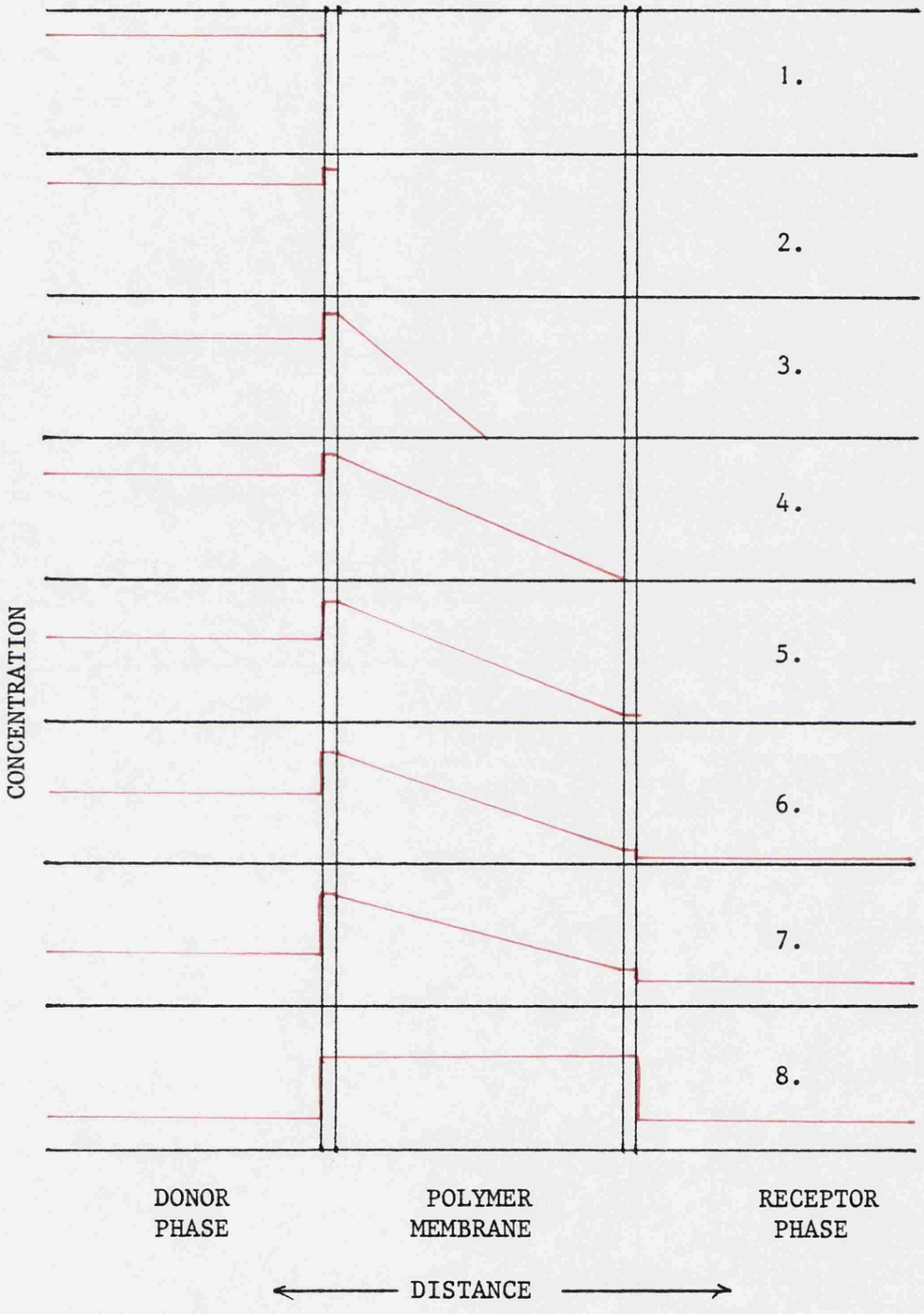


Figure 1.7 Schematic Representation of the Transport of a Solute Through a Polymer Membrane (Bray 1977)

This process has been shown to occur for the transport of many solutes of Pharmaceutical interest through polymeric films including polyamides (Ho 1977).

e) Desorption is a general term applied to the process whereby the net transfer of solute occurs from the sorbent back into solution. The term applies to the reverse of the adsorption, sorption and persorption processes. Many adsorption and sorption processes are reversible when physical forces are responsible for the immobilisation of solute. Consequently, if the equilibrated sorbent is placed in contact with a solvent, of lower chemical potential with respect to the solute, the system will re-equilibrate. The re-equilibration of the system will result in solute leaving the sorbent, although the point at which the equilibrium of the sorption system is re-established should also fall on the sorption isotherm (see section 1.5.1). The superimmposition of isotherms obtained from sorption and desorption experiments has been reported for the interaction of ethyl 4-aminobenzoate with nylon 6 (Richardson 1973, Ho 1977) and for 4-nitrophenol and active carbon (Mattson and Mark 1971).

1.5 EQUILIBRIUM SORPTION FROM SOLUTION

Adsorption at the solid liquid interface occurs in an attempt to reduce the interfacial tension of the solid adsorbent material when in contact with a solution. Dilute aqueous solutions of pharmaceutical importance generally consist of a solute, usually of limited solubility, dissolved in an excess amount of solvent.

The solute, usually a weak organic acidic or basic drug, is preferentially adsorbed at the interface with the sorbent whereas

the aqueous solvent molecules tend not to show a significant surface excess concentration. This type of sorption system is referred to as solute adsorption where the surface active properties of the solute are of direct interest. While the importance of the interaction of the solute with the solvent in bulk solution should not be overlooked, the overall behaviour of dilute solution adsorption can be considered analogous to adsorption from the gas phase. Indeed the development of models of sorption from solution were derived in many cases from those initially applied to gaseous sorption systems.

1.5.1 The Measurement and Representation of the Sorption Process.

If a dilute solution is placed in contact with a sorbent such that preferential sorption of the solute occurs, its concentration in solution will be reduced as sorption proceeds. The equilibrium uptake, or invariant adsorption (Radke and Prausnitz 1972b), which is equivalent to the surface excess of solute, can be determined by measuring the concentration change of the solution and application of the conservation of mass equation (equation 1.1).

Sorption data is typically represented using adsorption isotherms which are a plot of equilibrium uptake as a function of equilibrium concentration. The isotherm represents the sorption equilibrium of the solute from a particular solvent under specified physical conditions, and is independent of the dimensions of the experimental system from which it is measured.

$$n = \frac{V.\ \Delta C}{m} \quad \text{.....(1.1).}$$

where n = equilibrium uptake per unit weight of solid

V = solution volume

ΔC = the concentration change per unit volume due to contact with the sorbent

m = the sorbent mass

1.5.2 Classification of Adsorption Isotherms.

The shape of the isotherm is dependent upon the nature of the solute, solvent and sorbent. Giles (1960) recognised four types of isotherm which showed characteristic shapes in the initial slope region which were designated H, L, S and C. These four main sub-classes were further subdivided according to the variation in slope at higher uptakes. The Giles classification is summarised in figure 1.8.

1.5.2.1 L Type Isotherms.

L isotherms are characterised by a slope whose gradient decreases as the concentration of solute in the system increases, indicating that the number of "sites" available for sorption is limited. This type of behaviour is characteristic of non-specific interactions between solute and sorbent.

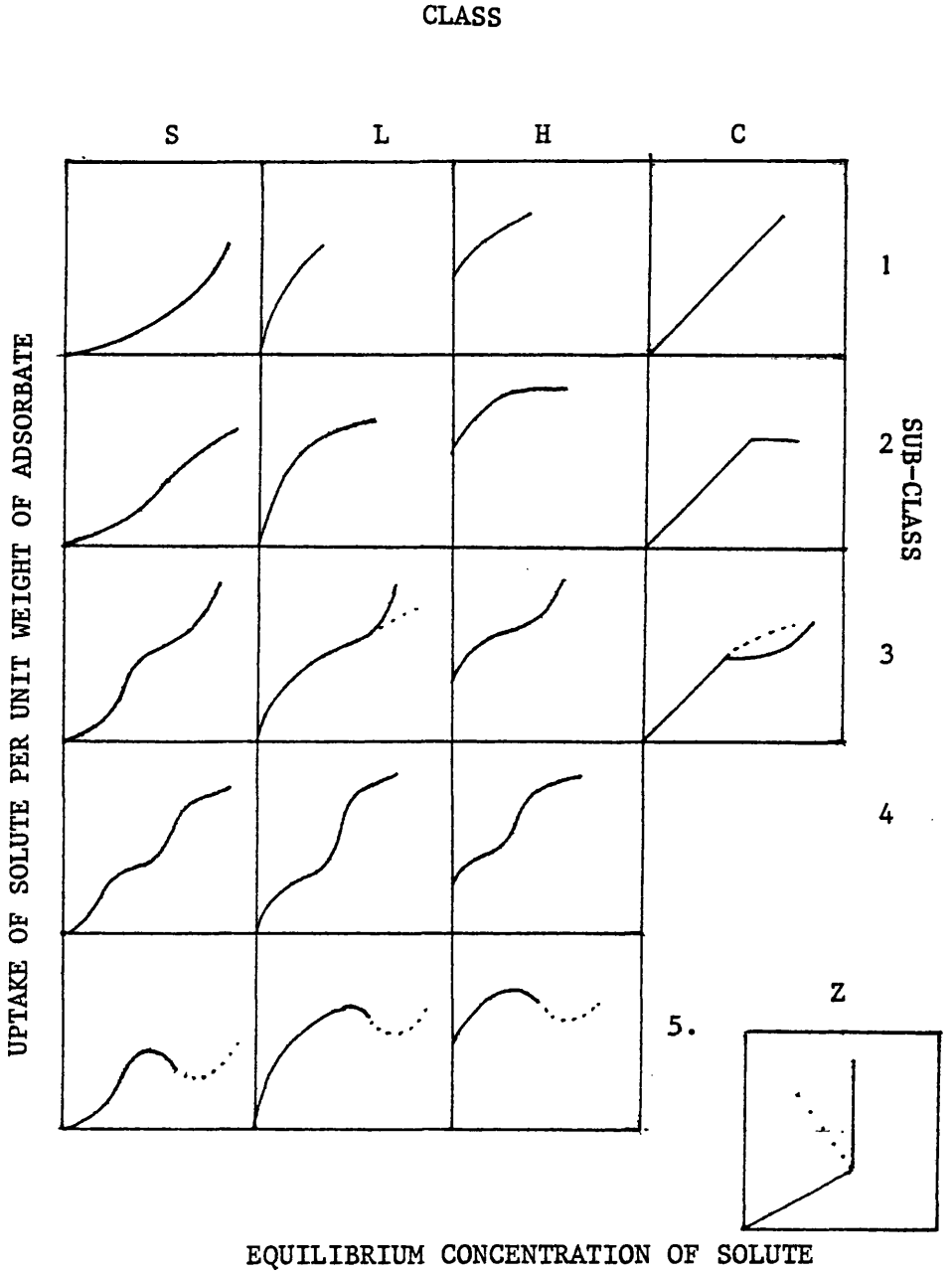


Figure 1.8 The Giles Classification of Sorption Isotherms.

The sorption of weak organic acids and bases from aqueous solutions on to active carbon generally give rise to L type isotherms. The following drug solutes give L isotherms for sorption by active carbon; chlorpheniramine maleate (Cooney 1978), emetine, pepsin (Cooney 1980) paracetamol, aspirin, salicylamide and phenyl-propanolamine (Tsuchiya and Levy 1972). Many other solutes have also been shown to give L isotherms on active carbon including benzoic acid (Kipling 1972), phenol and 4-nitrophenol (Jossens and Prausnitz 1978), other substituted phenols (Coughlin and Ezra 1968) and sodium benzenesulphonates (Weber and Morris 1964a).

A number of theoretical models have been developed to quantitatively describe L type behaviour. The earliest studies on adsorption from solutions were carried out by Freundlich who investigated the interaction of phenols and aliphatic acids with active carbons from dilute aqueous solution (Kipling 1965). The isotherms arising from the sorption system were L type in nature and the isotherm data were fitted to an empirical logarithmic expression (equation 1.2).

$$n = a.C_{eq}^{(1/m)} \quad \text{.....(1.2).}$$

where a = constant

m = constant $(1 > m > 0)$

n = equilibrium uptake per unit weight of sorbent

C_{eq} = equilibrium concentration mols l^{-1})

This equation was found to hold for small solute concentration ranges but does not account for the plateau which arises in L type systems at higher concentration (L type isotherms). Langmuir developed a model for adsorption on to sorbent surfaces from which the familiar Langmuir adsorption isotherm equation was derived (equation 1.3).

$$n = \frac{n_{max} \cdot b' \cdot C_{eq}}{1.0 + b' \cdot C_{eq}} \qquad \ldots\ldots\ldots (1.3)$$

where n = equilibrium uptake per unit weight of sorbent

C_{eq} = equilibrium concentration (M)

n_{max} = the value of uptake at which site saturation occurs (mol Kg^{-1})

b' = the Langmuir constant which is a function of adsorption energy

The Langmuir model for ideal adsorption makes the following assumptions (Langmuir 1917).

1) The adsorption surface is two dimensional and is composed of a "patchwork" of energetically homogeneous adsorption sites.
2) The energy of adsorption is unaffected by the extent of surface coverage
3) Adsorption is a dynamic process where at equilibrium, the rate at which solute molecules arrive at and depart from the surface is equal.
4) Lateral interaction between adsorbed molecules occupying adjacent adsorption sites is negligible.

The Langmuir equation can be used to fit L isotherm data as the functional form of the relationship takes into account the presence of the plateau.

The Langmuir model emphasises the solute interaction but the solvent is not taken into consideration. An alternative model for surface adsorption based on an ideal adsorbed solution has been developed, which is referred to as the "phase exchange" model (Everett 1964). This model was originally proposed to account for the appearance of maxima in isotherms when the interaction of the solvent with the sorbent becomes significant in more concentrated solution systems. It has been shown, however, that this would also describe Langmuirian adsorption behaviour as a special limiting case. (Everett 1979). The phase exchange model assumes that solute and solvent molecules adsorb together to give rise to an adsorbed ideal solution which has a different composition from the bulk aqueous solution. The equilibrium state of the composition of each solution is given by the law of mass action equation (equation 1.4).

$$K = \frac{X_1^a X_2}{X_1 X_2^a} \qquad \text{.....(1.4)}$$

where K = the phase exchange equilibrium constant

X_1^a = the solute mole fraction in the adsorbed solution phase

X_2^a = the solvent mole fraction in the adsorbed solution phase

X_1 = the bulk phase mole fraction of solute

X_2 = the bulk phase mole fraction of solvent

For dilute solution adsorption, the value of K is high indicating that preferential sorption of the solute takes place, with the consequent displacement of solvent to ensure that equation 1.4 is satisfied. The relationship in equation 1.4 is used to derive an expression which has a general Langmuirian form (equation 1.5).

$$n = \frac{n^a . X_1 . X_2 (K-1)}{1.0 + (K-1)X_1} \qquad \text{.....(1.5)}$$

where n = equilibrium uptake per unit weight of sorbent mol kg^{-1}

n^a = the total number of solute and solvent molecules adsorbed per unit weight of sorbent.

In the special case of dilute solution adsorption

$(K-1) \cong K$ .....(1.5a)

$X_2 \cong 1.0$ .....(1.5b)

$n^a \cong$ the number of solute molecules adsorbed .....(1.5c)

$X_1 \cong$ the molar concentration of solute .....(1.5d)

Comparison of equations 1.4 and 1.5 show that the two different models give rise to similar adsorption isotherm equations. The essential features of the mathematical characteristics of the Langmuir and Freundlich equations have been discussed with respect to their suitability to describe L type behaviour (Frangiskos et al 1961). The Freundlich equation does not account for plateau formation and the slope at the origin is infinite, whereas, the Langmuir equation will describe a plateau uptake the value of which is related to the initial slope. Frangiskos considered that a more satisfactory fitting of experimental data could be obtained using a three constant model. A recent study for the sorption of simple organic molecules with active carbon has led to the development of a potentially useful, three constant model (Radke and Pransnitz 1972a). If sorption is assumed to take place on a Langmurian surface, at low concentration the number of available sites greatly exceeds the number of solute molecules. In this situation Henry's law is obeyed and the extent of sorption is a linear function of the activity of the solute in the bulk solution. At a higher degree of occupation the slope of the isotherm starts to decrease as partial site limitation arises and an L_1 isotherm results which can be fitted by the Freundlich expression, given in equation 1.2. As the extent of uptake approaches the limit of sorption capacity, a fully developed L_2 isotherm arises characterised by a plateau. Radke proposed a semi-empirical equation (equation 1.6) which is capable of describing all types of L isotherm behaviour.

$$n = \frac{\alpha . C_{eq}}{1 + \frac{\alpha . C_{eq}^{(1-\gamma)}}{\beta}} \qquad \text{.....(1.6)}$$

where n = equilibrium uptake per unit weight of sorbent

C_{eq} = equilibrium concentration (M)

and α, β, γ are constants

At low concentration, equation 1.6 reduces to a statement of Henry's Law where uptake is solely a function of the bulk solution concentration and a distribution constant

$$\lim_{C_{eq} \to 0} \bar{n} = \alpha . C_{eq} \qquad \text{.....(1.6a)}$$

At higher concentration, equation 1.6 takes the form of the Freundlich equation which is similar to equation 1.2

$$n = \beta . C_{eq}^{\gamma} \qquad \text{.....(1.6b)}$$

In the special case where $\gamma = 0$ an equation of the Langmuir type, equivalent to equations 1.3 and 1.5 arises.

$$n = \frac{\alpha . C_{eq}}{1.0 + \alpha . C_{eq}/\beta} \quad \text{.....(1.6c)}$$

The most widely used isotherm equations in the literature appear to be the Langmuir and Freundlich equations. The Radke equation seems, however, to be of use for the overall description of generalised L type isotherm behaviour.

1.5.2.2. H Type Isotherms.

The H isotherm is a special case of L type behaviour characteristic of sorbents which have a high affinity for the solute.

At low concentration, the solute is effectively removed from solution with the result that the isotherm appears to originate from the uptake axis. The sorption of promazine on active carbon from water has been shown to be of the H type. (Sorby et al 1966). H isotherms also arise due to the strong charge transfer interations typically occuring in the sorption of ions by ion exchange resins (Giles 1960).

1.5.2.3 S Type Isotherms.

The S isotherm is characterised by an apparent increase in the number of available adsorption sites with increasing surface occupation. In many cases the S isotherm indicates that a

"co-operative adsorption" mechanism is operating where solute molecules are adsorbed in rows or clusters in an edge-on orientation.

This type of sorption behaviour is typically shown by monofunctional amphiphilic solutes adsorbing on to metal oxide sorbents (Giles et al 1974) although the sorption of caproic acid by active carbon also gives rise to S type behaviour (Meier et al 1972). The co-operative adsorption mechanism is illustrated schematically in figure 1.9.

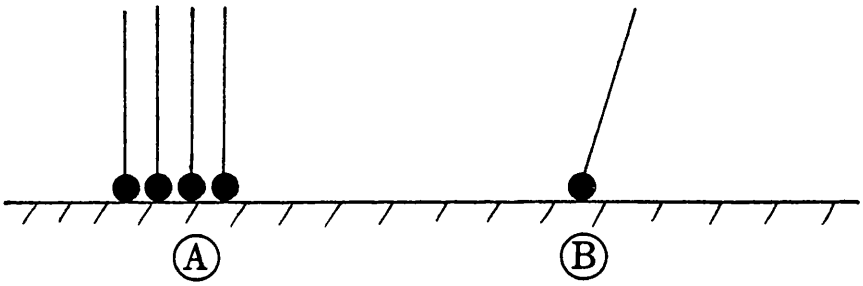


Figure 1.9 Schematic Representation of Co-operative Adsorption.

The monofunctional amphiphilic solute can bind in an upright orientation as the solvophobic moeity associates with the surface while the solvophilic moeity remains solvated by the bulk solution.

If a lateral physical or steric interaction can take place between adjacent molecules in the adsorbed phase, the solute molecule at position A in figure 1.9 will be stabilised at the surface to a greater extent than the solute molecule at position B. As an increasing degree of site occupation gives rise to a consequent

increase in stabilisation, an S isotherm would be expected to arise in this case. S isotherms are also shown in systems where the solvent or trace contaminants adsorb in preference to the solute (Giles et al 1974).

Fundamental studies into the sorption of 4-nitrophenol on to silica dust indicates that L_2 isotherms arise from sorption from benzene. The S isotherms occur when trace quantities of water are present in the benzene and uptake is completely abolished when water replaces benzene as the solvent.

Although effectively taking place on a Langmuirian surface, the lateral interaction is inconsistent with the Langmuir model, therefore, S type behaviour is not represented by equation 1.3 or its associated functional relationships.

1.5.2.4. C Type Isotherms.

The C isotherm is linear and is typically shown in sorption systems where the solute is capable of pentrating the sorbent. This type of isotherm is typically found where polymeric sorbents are used.

The sorption of a group of parasubstituted benzoic acid and ethylbenzoate derivatives show C type behaviour when sorbed by nylon 6 (Richardson 1973) and the sorption of ethyl 4-aminobenzoate by nylons 6, 11 and 12 similarly gives rise to this type of isotherm (Ho 1977).

C isotherm behaviour has been the subject of a review where three possible sorption mechanisms have been discussed (Giles et al 1964). Firstly the polymeric sorbent may be considered to behave as a "supercooled" liquid into which the solute partitions (Richardson 1973). Sorption, in this case, continues until the plastic matrix becomes saturated whereupon sorption ceases abruptly signified by

the appearance of a plateau. The subclass of C type isotherm behaviour where a plateau arises is referred to as C_2 type behaviour. Alternatively, interactions showing linear isotherms are considered as being in an early stage of L type behaviour where Henry's Law is obeyed. In this case, limitation of linear behaviour would appear as a gradual change from a C to L type isotherm and an abrupt cessation of sorption associated with the appearance of a plateau would not occur. A further approach suggested by Giles, involves a mechanism of solute induced matrix disruption. Solute molecules disentangle the polymer chains as sorption proceeds resulting in the exposure of a greatly increased number of sorption sites which will always exceed the number of remaining solute molecules attempting to interact. This model may account for the observation that certain solutes such as phenol will plasticize or dissolve nylon 6 (Autian 1963). A special limiting case would result in this instance if the solute is capable of inflicting gross damage on the polymer matrix. This special case of C type behaviour, giving rise to a Z isotherm (figure 1.10) has been observed for the non-equilibrium sorption of 4-nitrophenol on to cellulose from an organic solvent (Giles and Tolia 1964).

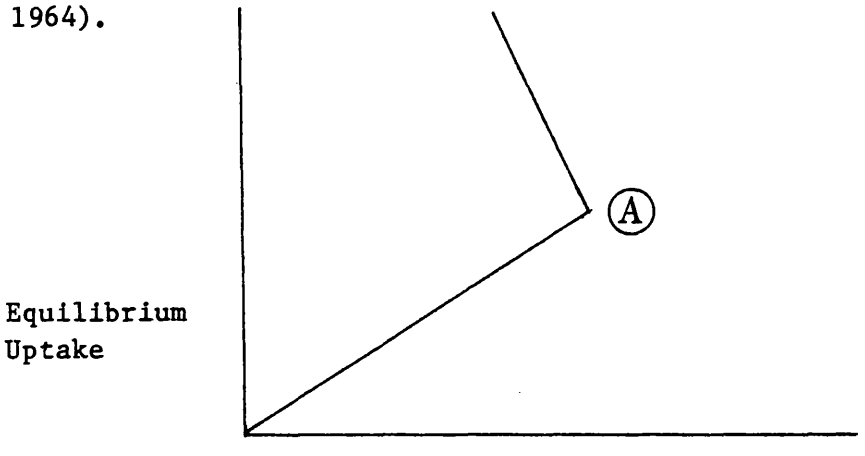


Figure 1.10. Schematic Representation of the Z Type Isotherm.

The solute penetrates the sorbent by a process of controlled disentanglement, giving rise to a C isotherm until a certain critical uptake is reached whereupon gross damage to the polymer structure takes place. This results in a large increase in sorption, indicated by letter A in figure 1.10, due to the instantaneous exposure of many more sites which are capable of interacting with the solute.

The gradient of the isotherm, or K value, defines the position of the equilibrium for C type behaviour as the extent of uptake of the solute is directly proportional to the equilibrium concentration of drug in solution, that is

$$K = \frac{n}{C_{eq}} \qquad \text{.....(1.7)}$$

where n = equilibrium uptake per unit weight of sorbent

C_{eq} = equilibrium concentration (M)

K = the sorption or affinity constant

1.5.3 Factors Affecting the Equilibrium Sorption of Solutes from Solution.

The position of the equilibrium in an adsorption process will depend upon the relative affinity of the solute for the sorbent and the solvent. The equilibrium will, therefore, change as a result of alteration in the nature of the solute, sorbent or solvent or physicochemical changes likely to alter either the solute-solvent or the solute-sorbent interaction or both.

1.5.3.1 The Morphology and Chemical Nature of the Sorbent.

The structure of the sorbent will influence the tendency of a given solute to associate with or diffuse within itself. In addition to structural considerations, certain chemical groupings present in the sorbent may act as specific sites on to which solute molecules may bind.

1.5.3.1.1 Active Carbon

The sorption characteristics of active carbon are determined by the activation process which produces the pore structure and nature of the surface. The influence of pore structure on the sorption of acetic and valeric acid has been investigated using a range of active carbon granules which were activated over periods of one to eight days (Lemieux and Morrison 1947). The surface area determined from the sorption of acetic acid was 60% greater than that determined by valeric acid after one day of activation, whereas after eight days only a 9% difference in area was apparent. It was suggested that the pore structure was less accessible to the larger valeric acid molecule, initially, due to a molecular sieve effect which was abolished as the pore structure was enlarged and consolidated after prolonged activation.

The carbon surface is composed of carbon atoms arranged in turbostratic configuration modified in places by chemisorbed oxygen.

From sorption studies carried out into the effect of activation on the uptake of inorganic bases it was concluded that two types of carbon surface can arise. (Steenberg 1944). Carbons activated at low temperature (L carbons) were shown to adsorb inorganic bases, whereas, those activated at higher temperatures (H carbons) did not. Further studies into the uptake of organic solutes from organic solvents by H and L carbons have shown that selectivity may occur as a result of different activation temperatures. L carbons appeared to preferentially adsorb polar solutes from organic solvents (Bartell and Lloyd 1938) whereas H carbon preferentially adsorb non polar species (Kipling 1956). In contrast to these findings, sorption studies using fatty acid solutes from aqueous solution revealed that the uptake characteristics were independent of the chemical nature of the surface and depended only upon the available surface area (Linner and Williams 1950).

1.5.3.1.2 Nylon 6

Preliminary studies carried out into the interaction of drug solutes with polymers commonly used in Pharmacy and Medicine demonstrated that the presence of specific chemical groups in the matrix was essential for the binding of benzoic acid derivatives which were sorbed by nylons but not polyethylene or polystyrene (Kim and Autian 1960). The role of the amide group was further emphasised where investigations into the sorption of ethyl 4-aminobenzoate by various nylons indicated that the K value was correlated with the amide frequency (Richardson 1973). The amide frequency describes the relative proportion of amide groups to methylene groups in the matrix.

The hydrophilic nylon 6 matrix possesses three amide groups per 22 chain carbon atoms as does the copolymer nylon 6:6. The more hydrophobic nylons 11 and 12, however, possess three amide groups per 32 and 34 chain carbon atoms respectively. The sorption of water by nylon polymers has also been shown to correlate with amide frequency (Puffr and Sebenda 1967). The effect of changes in amide frequency has been suggested to affect sorption either by a modification of the abundance of binding sites or by an indirect effect whereby the extent of matrix swelling, brought about by hydration, is modified (Richardson 1973).

Further evidence for the hypothesis that matrix swelling is involved in the sorption process has been obtained from thermodynamic studies of the interaction of ethyl 4-aminobenzoate with nylons 6, 11 and 12. Van't Hoff plots for the sorption process show points of inflexion at 45^{o}, 42^{o} and 42^{o} for nylons 6, 11 and 12 respectively which have been attributed to the effect of secondary standard phase changes on sorption (Ho 1977). Comparison with the phase transition determined from differentialscanning calorimetry (Lord 1974) reveals that the nylon 6 transition temperature at 61^{o} is inconsistent with the sorption studies, however, close agreement occurs with nylons 11 and 12 with transition temperatures of 40^{o}. The difference in the transition temperature for nylon 6 measured by the two techniques suggests that its matrix may be hydrated and therefore plasticized to a greater extent that the relatively more hydrophobic nylons 11 and 12. The sorption of ethyl 4-aminobenzoate by nylon 6 powder and film has also been shown to be different (Richardson 1973) which has been attributed to a dissimilar crystallinity in the two matrices.

1.5.3.2. The Nature of the Adsorbate.

The nature of the solute has an effect both on the solute-solvent and solute-sorbent interactions. In general a solute is adsorbed to a greater extent from a "poor" solvent than a "good" one, therefore, any alteration in substituents for a given class of chemical compounds which results in a reduction in solubility will subsequently enhance the extent of uptake and vice versa. If a specific interaction occurs between a particular chemical compound and adsorption sites on the sorbent surface, substitution of the solute molecule may alter the nature of the solute-sorbent bond or association with a resultant change in the overall sorption process. The effect of substitution may also affect both the solute-solvent and solute-sorbent interactions.

1.5.3.2.1. Active Carbon

The structure-activity relationships governing the sorption of organic solutes by active carbon from aqueous solution have been the subject of several recent studies. The uptake of fatty acids by active carbon has been shown to increase with the methylene chain length in a homologous series (Adamson 1967). This type of behaviour is said to obey Traube's rule which states that "the adsorption of organic solutes from aqueous solution increases strongly and regularly as a homologous series is ascended". If the isotherm of members of the homologous series are plotted as equilibrium uptake versus reduced concentration, the resulting profiles have been shown to superimpose (Hansen and Craig 1954). Reduced concentration is defined as the solute concentration divided by the saturation solubility at the temperature of the isotherm determination. It has further been

suggested that if the reduced concentration profiles superimpose the intensity of the solute-sorbent interaction for each member of the series is identical (Lemieux and Morrison 1947). More recent studies have indicated that the general sorption solubility hypothesis implied by the use of Traube's rule does not hold in all cases of substitution. The principles of Traube's rule could be applied to the sorption of 3-substituted benzoic acid derivatives by active carbon, but not a 2-substituted series (Komori and Urano 1974). It was suggested that complex electronic effects associated with ortho substitution resulted in the apparent non-ideal behaviour with respect to Traube's rule, and that instead, substitution modified a specific interaction between the sorbent and the aromatic electron ring of the solute. The effect of substitution on specific solute-sorbent bonding has also been investigated by comparing the infra-red spectrum of solute molecules in the free and adsorbed state (Mattson & Mark 1971). Consideration of the spectrum indicates that the functional group substituents of bound phenolic derivatives were unperturbed suggesting that the solute-sorbent bond primarily involved the π electron cloud of the solute confirming the result of Komori. The effect of substitution in this case was twofold, firstly modifying solubility and secondly, modifying the solute-sorbent interaction either by enhancing or depleting the aromatic π cloud electron density.

1.5.3.2.2. Nylon 6.

The effect of solute structure on the sorption of chemically related compounds by nylons 6 and 6:6 has been the subject of extensive study. A linear relationship between the logarithm of the

K value of a series of carbamate, acetanilide and aniline derivatives and the logarithm of their aqueous solubility has been established for sorption on to nylon 6:6 (Ward and Upchurch 1965). A similar study using polyamide thin layer chromotography confirmed this result, where a linear relationship was observed using R_f and R_m values for structurally related phenolic derivatives in place of the sorption K value (Bark and Graham 1967). An investigation into the solubility dependence of the K values for a series of 4-substituted benzoic acid derivatives on nylon 6 demonstrated that certain compounds do not conform to the general prediction of uptake based on solubility considerations (Richardson 1973). Substitution of benzoic acid by methoxy, nitro, fluoro, bromo, acetyl and cyano groups confirmed that as solubility decreases, the sorption constant increases and that the logarithms of solubility and the K value are linearly related. The 4-chloro and hydroxy derivatives and benzoic acid itself fell above the ideal line indicating that their uptake was higher than would be predicted from solubility considerations. It was suggested that certain functional groups, such as the phenolic-OH group, may confer on the solute the ability to form specific bonds with nylon, whereas solutes not possessing this type of functional group simply associate non-specifically by Van-der-Waals' forces. Further evidence for the existence of specific hydrogen bond has been obtained by substituting bulky functional groups into the phenol nucleus in the 2 and 5 positions (Bark and Graham 1967 Kim and Autian 1960). Substitution in these positions led to a reduction in the sorption of phenolic derivatives indicating that the formation of a specific bond between the amide linkage and phenolic group could be prevented by steric hinderance.

1.5.3.3. pH.

The sorption of weak acids and bases by non-ionic sorbent materials is generally dependent upon the relative concentration of solute in the ionised and unionised forms. The relative species concentration is related to the pH of the solution and pK_a of the solute (for a monoacid or monobasic species) by the Henderson - Hasselbalch equation (equation 1.8) shown below for a weak acid.

$$pH = pk_a + \log \frac{[salt]}{[acid]} + \log \gamma \quad \ldots\ldots\ldots\ldots (1.8)$$

where γ = the activity coefficient.

If the extent of sorption is dependent upon the state of ionisation of the solute equation 1.8 would indicate that the variation will occur within the limit of the solute $pK_a \pm 2$ pH units. Generally sorption tends to increase as the concentration of the solute in the unionised form increases.

1.5.3.3.1 Active Carbon

The sorption of 3-dodecylbenzenesulphonate by active carbon has been shown to increase below pH 4 (Weber and Morris 1964b). Organic aromatic sulphonates are strong acids and as such ionisation of the solute is unlikely to affect the extent of sorption. Instead, it was suggested that charge neutralisation of ionisable functional groups on the sorbent surface accounted for increased sorption by the carbon. An investigation of the effect of pH on the sorption of 3,6-dichloro-2-methoxybenzoic acid has shown that the extent of uptake is proportional to the concentration of the unionised form of the solute. The sorption profile for this system (figure 1.11) also shows that significant adsorption of the ionised species takes place (Getzen and Ward 1969).

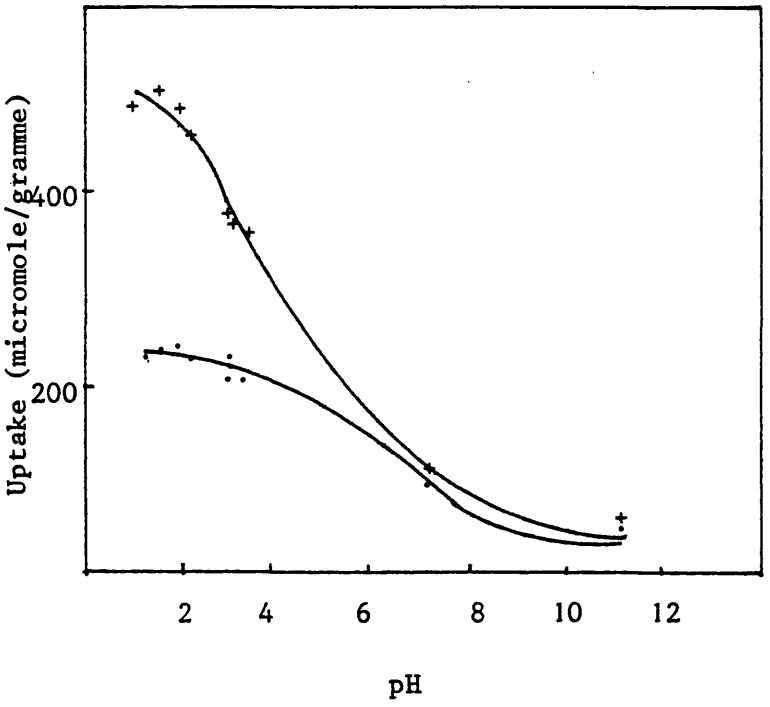


Figure 1.11 pH Profile for the Sorption of 3,6-dichloro-2-methoxybenzoic acid on Active Carbon.

	Initial Concentration (mole/litre) x 10^4
+	1.00
·	0.25

1.5.3.3.2 Nylon 6.

The effect of pH on the sorption of ionisable solutes by nylons have been demonstrated using ethyl 4-aminobenzoate and nylon 6 (Richardson 1973, Ho 1977) and salicylic acid and nylon 6:6 (Kapadia et al 1964). The sorption of ethyl 4-aminobenzoate was at a maximum value when the solute was fully unionised and was half this maximum value at a pH corresponding to the pK_a. There was no apparent sorption when the solute was fully ionised indicating that the solute cannot interact with the nylon sorbent in a fully ionised state. The pH-sorption profile obtained from this study is shown in figure 1.12.

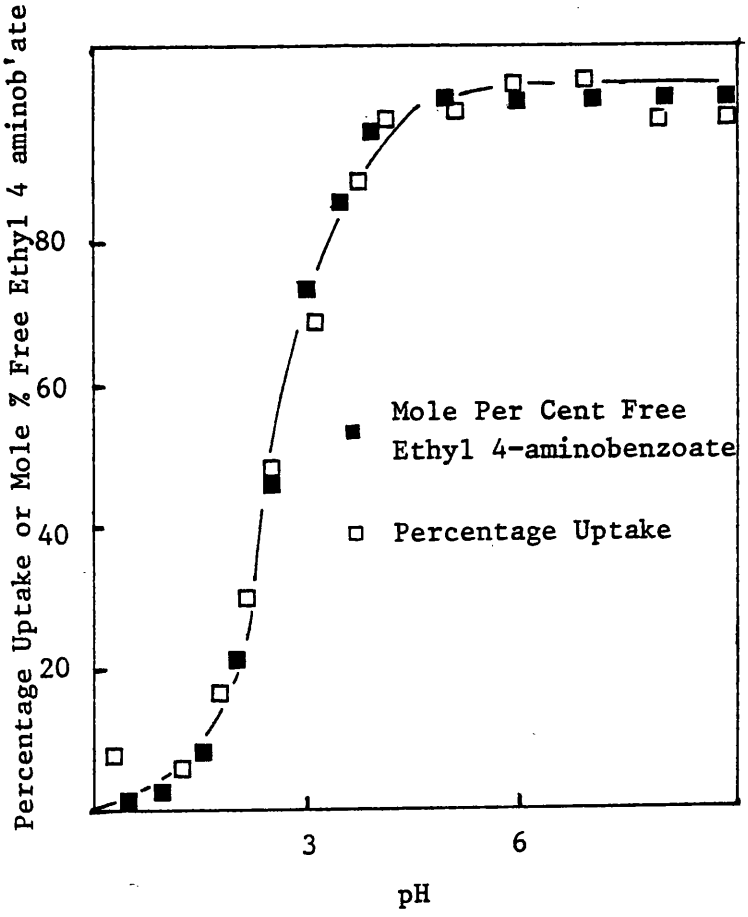


Figure 1.12 pH Profile for the Sorption of Ethyl 4-aminobenzoate by Nylon 6 from Buffered Solutions of Constant Ionic Strength and Constant Temperature.

The apparent similarity between the sorption : pH profile and the dissociation curve further emphasises the dependence of the sorption process on the state of ionisation of the solute.

1.5.3.4. The Effect of Temperature on Adsorption from Solution.

As the temperature of an adsorption system rises, a reduction in affinity and capacity of the adsorbent for the adsorbate is generally apparent. This corresponds to a weakening of attractive forces between the solute and adsorbent and an increase in solubility of the solute in the solvent. The equilibrium will thus be displaced in favour of the solution as temperature rises, the extent of which will depend on the temperature coefficient of solute affinity for both.

1.5.3.4.1 Active Carbon.

Extensive study of the thermodynamics of adsorption from solution has been undertaken particularly with respect to adsorption from concentrated solutions (Kipling 1965). The effect of temperature on the sorption of solutes from dilute solution on to active carbon has, however, received comparatively little attention. As active carbon sorbents generally show L type behaviour it is necessary to represent the sorption equilibrium using model equations with more than one constant. In this case a simple relationship such as the Van 't Hoff isochore cannot be used to predict the effect of temperature on the overall sorption process. Studies of the sorption of 4-nitrophenol by active carbon have attempted to use the reduced concentration uptake profile to predict the overall effects of temperature on the adsorption process (Mattson & Mark et al 1971). It was assumed that the L type isotherm at any temperature could be predicted from the reduced concentration plot provided that the saturation solubility was known

at all temperatures. Poor agreement with experimental data was found using this method which led the authors to assume that temperature affected both the solute-sorbent interaction as well as solubility, in which case the prediction method based solely on solubility consideration would not apply. This effect has also been reported for the adsorption of iodine on to non-porous carbon from cyclohexane (Kipling 1964). The isotherms for this system could be successfully predicted using the reduced concentration profile but, these findings were not supported by experiments using different solvents and various other non-porous carbon sorbents. The effect of temperature on the two Langmuir equation constants has been demonstrated by an investigation of the effect of temperature on the sorption of benzenesulphonates by active carbon. The process was found to be exothermic and the overall isotherm was displaced upwards as temperature decreased. The affinity constant (b' in equation 1.3) was apparently temperature independent whereas the plateau uptake (n_{max} in equation 1.3) was influenced by temperature. In this special case the variation of plateau uptake could be predicted by a Van't Hoff plot based on equation 1.9 where n_{max} was used in place of K. A differential heat of adsorption was calculated from this plot with a value of -6.0 KJ mol^{-1}. The theoretical justification for and the exact significance of this parameter was, however, not discussed (Weber and Morris 1964a).

1.5.3.4.2 Nylon 6.

Temperature changes have also been shown to affect the matrix structure of polyamides due to a thermally induced realignment of interchain hydrogen bonds (Lord 1974). The effect of this structural realignment is also reflected in the sorption process (Ho 1977,

Richardson 1974). The effect of temperature on sorption of solutes by nylons has been studied using a conventional equilibrium thermodynamics approach. (Richardson 1977, Ho 1977, Autian 1963). The K value measured from the isotherm slope is approximately equal to the dimensionless equilibrium constant for dilute solution sorption systems (Richardson 1973). The standard entropy for sorption ΔS^{o} can be obtained from the linear isochore plots of ln K versus reciprocal absolute temperature, using the Van't Hoff equation.

$$\ln K = -\frac{\Delta H^{o}}{RT} + \text{constant} \quad \ldots\ldots\ldots\ldots (1.9)$$

where R = the universal gas constant

T = the absolute temperature

The sorption process is generally exothermic, consequently ΔH^{0} is negative. ΔH^{0} values for the sorption of benzoic acid derivatives by nylon 6:10 are of the order - 13 KJ mol^{-1} (Kapadia et al 1964) and values of -11 KJ mol^{-1} have been obtained for the sorption of benzoic acid derivatives by nylon 6 powder (Richardson 1973). The standard free energy change (ΔG^{o}) is obtained from equation 1.10 and the remaining thermodynamic parameter, the standard entropy of sorption, ΔS^{o}, follows from equation 1.11 the Gibbs equation.

$$\Delta G^{o} = -RT \ln K \quad \ldots\ldots\ldots(1.10)$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \quad \ldots\ldots\ldots(1.11)$$

The influence of temperature on the sorption of ethyl 4-aminobenzoate by nylon 6, 11 and 12 has been reported by Ho (1977) who showed that a point of inflexion occured in the Van't Hoff isochores, shown in figure 1.13

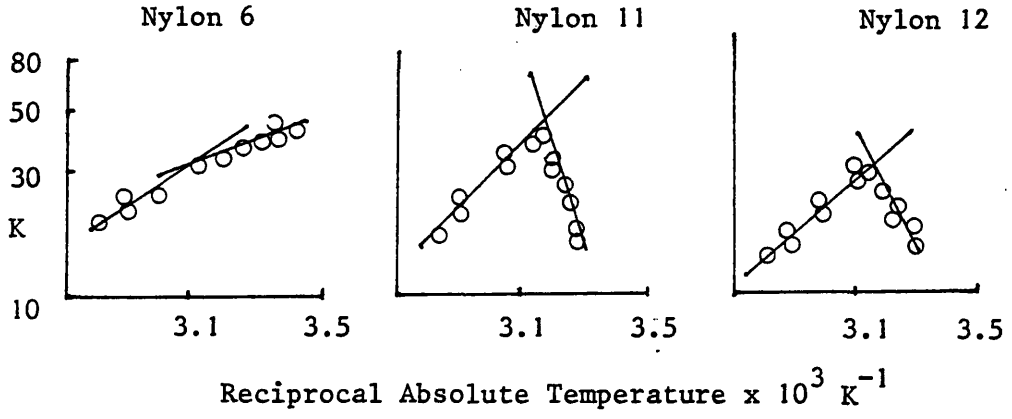


Figure 1.13 Van't Hoff Isochores for the Sorption of Ethyl 4-aminobenzoate by Nylons 6, 11 and 12.

It was suggested that the points of inflexion were associated with secondary phase transitions in the polymer as discussed previously (Ho 1977). For nylon 6 the ΔH^{o} values are exothermic in the temperature range above and below the inflexion temperature. ΔH^{o} values for nylons 11 and 12, however, change from endothermic at low temperatures to exothermic at higher temperatures. The data for nylon 6 was explained in terms of the increased segmental motion in the polymer at temperatures above the secondary phase transitions making binding sites more accessible. The interpretation of the data for nylons 11 and 12, however, remains unclear. These findings indicate that the effect of temperature on the sorption process is not restricted to the transfer of solute between the solution and polymer phases. Care should, therefore, be taken with regard to conclusions drawn from sorption thermodynamics studies concerning the energetic nature of the solute-polymer interaction. Several workers have used the thermodynamics parameters associated with the sorption process to assign specific bond formation mechanisms to the adsorbent-adsorbate interaction (Autian 1963, Rodell 1964). Later work has, however, refined the thermodynamic model to separate the solute dissolution effects from the experimental sorption process. A Hess relationship (equation 1.12) using thermodynamic parameters associated with the dissolution process to account for the adsorbate-solute interaction has been applied to the sorption of ethyl 4-aminobenzoate from a range of cosolvent solutions.

$$\Delta H^{o}_{\text{interaction}} = \Delta H^{o}_{\text{sorption}} - \Delta H^{o}_{\text{solution}} \quad \ldots\ldots\ldots (1.12)$$

The ΔH^{o} interaction parameter remained constant over a wide range of water-cosolvent concentrations, a result which would be anticipated if the thermal effects on the solvent phase were successfully eliminated (Richardson 1977).

1.5.3.5 Ionic Strength.

In many cases of adsorption from aqueous solution the influence of electrolyte concentration has been ignored. When a series of buffered solutions at difference pH levels are used, the ionic strength promotes adsorption by depressing the solubility of the solute in solution. Several workers have reported on the influence of ionic strength in the sorption of solutes indicating the control of the overall electrolyte concentration in sorption studies is essential.

1.5.3.5.1 Active Carbon.

The effect of electrolytes on the sorption of solutes by active carbon is similar to that for nylon 6 uptake. The addition of bromide and chloride ions was found to promote the sorption of benzoic acid by active carbon (Hasher 1963) and the adsorption of phenothiazine derivatives was similarly affected by the addition of sodium chloride (Sorby et al 1966).

1.5.3.5.2 Nylon 6.

The influence of ionic strength on the sorption of organic solutes by nylon 6 has been investigated by Richardson (1973). As the ionic strength increases, the solubility of the solute decreases and sorption is enhanced. A modification of the Sétchenov equation for the solubility of non-electrolytes, shown in equation 1.13 was proposed to account for the effect of electrolyte on the sorption of ethyl 4-aminobenzoate by nylon 6.

$$\log_{10} K = \log_{10} \frac{Sp}{So} + mc \qquad \ldots\ldots\ldots\ldots (1.13)$$

where K = sorption constant

Sp = "solubility" of the solute in the polymer

S_o = solubility of the solute in the solvent

m = empirical constant

c = salt concentration

A plot of the logarithm of the sorption constant versus electrolyte concentration was found to be linear and the value of Sp determined from the intercept showed close agreement with that determined experimentally.

1.6 DYNAMIC ADSORPTION FROM SOLUTION.

The rate at which a sorbent material depletes solute from solution is, in addition to the equilibrium adsorption characteristics, of major technical significance. The sorption interaction process has been subdivided into four stages which are summarised below (Klein 1980).

a) Diffusion of solute from the bulk solution to the proximity of the sorbent.

b) Diffusion of the solute across a concentrated, static film of solution at the geometric surface of the sorbent.

c) Sorption or persorption within the sorbent where solute is transported from the geometric boundary of the sorbent to internal adsorption sites.

d) Adsorption on to internal active sites following sorption or persorption.

If the static solute rich layer at the sorbent boundary is small or can be abolished by agitation of the solution, the sorption or persorption stage within the sorbent can be considered to be the rate limiting step. This step in the overall sorption process has been described as a diffusion process (Barrer, 1949) and measurement of parameters associated with this process have been used to characterise the kinetic properties of sorbents.

The theoretical model for diffusion assumes that the rate of mass transfer within the sorbent phase is proprtional to the concentration gradient of the solute, in the direction of mass flow, and the area available for diffusion. The basic equations describing the diffusion process were proposed by Fick (Crank 1975) and are given in equations 1.14 and 1.15.

$$F = \frac{dm}{dt} = -\bar{D}.A.\frac{dc}{dx} \quad \text{.....(1.14)}$$

$$\frac{dc}{dt} = \bar{D}.A.\frac{d}{dx}\left(\frac{dc}{dx}\right) \quad \text{.....(1.15)}$$

Continued .....

Continued . .

where F = flux

C = the concentration of solute in the diffusing medium

x = the distance co-ordinate in the direction of mass transfer

t = time

m = mass of solute transported

$\bar{D}$ = diffusion coefficient

The proportionality constant, $\bar{D}$, is known as the diffusion coefficient and is dependent upon temperature, the relative molecular dimensions of the solute and the "space" within the sorbent in which it is free to move. $\bar{D}$ is a useful parameter which is characteristic of the resistance of an adsorbent to mass transfer and is an indicator of overall sorption kinetics. The unit of $\bar{D}$ is $m^2\ sec^{-1}$, and the higher the value of $\bar{D}$, the faster solute can diffuse within the sorbent which results in a faster overall rate of sorption.

The expressions given in equation 1.14 and 1.15 apply to mass transfer and concentration change within the sorbent which are not measurable by direct experimentation. It is, therefore, necessary to solve equation 1.14 and 1.15 for an appropriate set of initial and boundary conditions. In many cases this requires isotherm data to enable mass flow within the sorbent to be measured by observation of the external solution concentration change. The approach to the measurement of $\bar{D}$ is identical for both polymeric and active carbon adsorbents. The experimental design of kinetics experiments and the solutions of equation 1.15 employed will however vary due to differences in their physical form, nature and sorption characteristics

1.6.1 Diffusion in Polymeric Sorbents.

The diffusion coefficient for the interaction of solutes with polymers can be measured by investigation of the rate at which solutes permeate through, or are sorbed by, polymeric films. Sorption rate studies using powdered polymeric material tend not to be used as, for example, the rate of sorption of ethyl 4-aminobenzoate is high resulting in the attainment of equilibrium within 2 to 3 minutes (Richardson 1973).

1.6.1.1 The Characterisation of Diffusion Using Membrane Permeability Experiments.

Permeability experiments consist of measuring the rate of appearance of solute in a solvent, separated from a concentrated solute solution by a polymer membrane. The concentration distance profile for this system is shown schematically in figure 1.14 Equation 1.15 has been solved for non steady state conditions the donor solution concentration (C_D^s) and the receptor solution concentration (C_R^s) remain constant and effectively zero, respectively, throughout the determination and the polymer is initially free of solute (Crank 1956, Barrer 1939). The solution, given in equation 1.16, takes the form of a function relating the mass present in the receptor solution as a function of time.

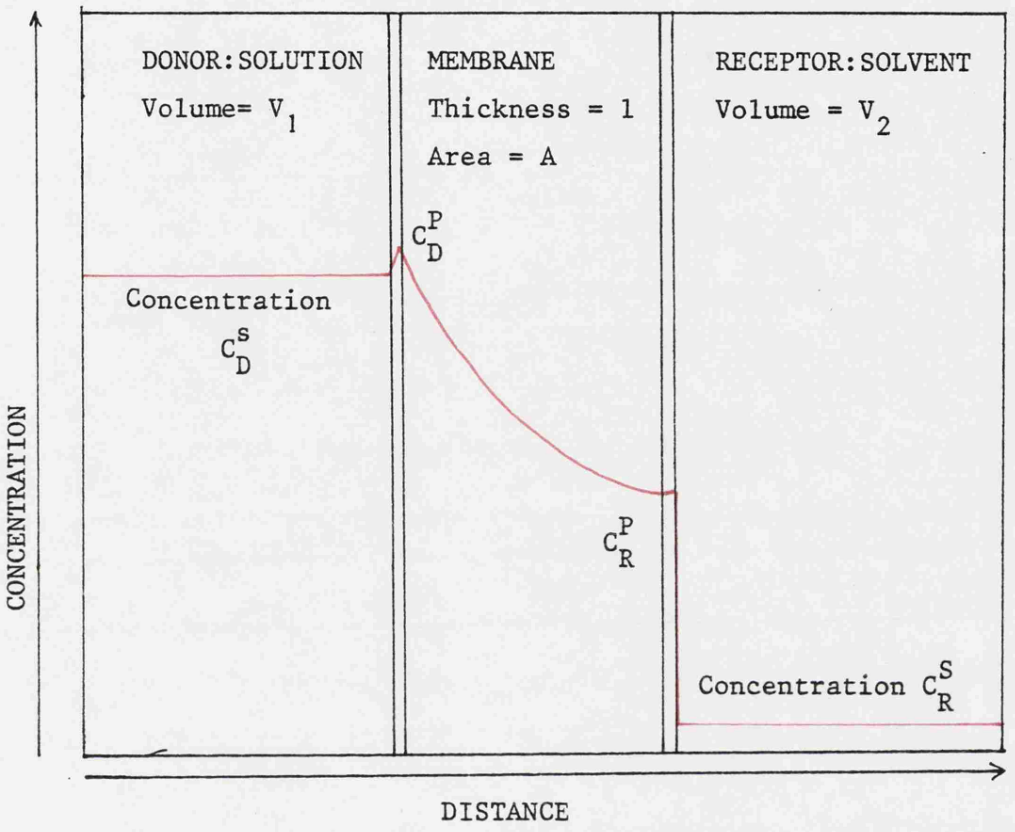


Figure 1.14 Diffusion Profile for Permeation Through a Polymer Membrane

where C_D^S = the donor solution concentration

C_R^S = the receptor solution concentration

C_D^P = the solute concentration within the donor interface of the membrane

C_R^P = the solute concentration within the receptor interface of the membrane

$$Q_{(t)} = \left(\frac{\bar{D}.A.t.C_D^P}{\ell}\right) - \left(\frac{\ell.A.C_D^P}{6}\right) - \left(\frac{2.\ell.C_D^P}{\pi^2 D}\right) \sum_{n=1}^{\infty} \frac{(-1)^n}{2} \text{EXP} \frac{(\bar{D}n^2\pi^2 t)}{\ell^2} \quad \ldots\ldots(1.16)$$

where $Q_{(t)}$ = diffusing mass present in receptor phase at time, t.

ℓ = membrane thickness

A = membrane area

C_R^P = the solute concentration within the receptor interface of the membrane.

As time approachs infinity the series exponential term in equation 1.16 is eliminated and simplifies to equation 1.17.

$$Q_{(t)} = \left(\frac{\bar{D}.A.t.C_D^P}{\ell}\right) - \left(t - \frac{\ell^2}{6\bar{D}}\right) \quad \ldots\ldots\ldots(1.17)$$

The function of $Q_{(t)}$ versus t is now linear with an intercept on the abscissa referred to as the lag-time. Equation 1.18.

$$\text{Lag-time} = \frac{\ell^2}{6\bar{D}} \quad \ldots\ldots\ldots(1.18)$$

Equations 1.16 - 1.18 indicate that the plot of $Q_{(t)}$ versus time would take the form of that shown schematically in figure 1.15 the so-called Barrer Plot.

The $Q_{(t)}$ versus time profile shown in figure 1.15 has been obtained for several experimental solute-nylon permeability determinations of pharmaceutical interest, and has been used in conjunction with equation 1.18 to obtain $\bar{D}$ as the membrane thickness can be measured and the lag-time can be determined from direct experimentation.

The $\bar{D}$ value, and a further constant representing permeability, the permeability coefficient (P) can be obtained from the steady-state slope of the Barrer plot (Rodell et al 1966, Crank 1956). Under steady state conditions equation 1.19 arises directly from equation 1.15

$$\frac{dm}{dt} = \frac{-\bar{D}.A.\ (C_D^P - C_D^P)}{\ell} \qquad \text{.....(1.19).}$$

If the sorption isotherm is linear and $\bar{D}$ is independent of concentration in the polymer, the polymer concentration terms in equation 1.19 can be replaced by concentrations in the donor and receptor phases using the C isotherm relationship given in equation 1.15 (Ficks second law) which is rewritten in equation 1.20

$$K = \frac{C_D^P}{C_D^S} = \frac{C_R^P}{C_R^S} \qquad \text{.....(1.20).}$$

If the permeability determination is carried out under sink conditions such that C_R^S is effectively zero; equation 1.20 can be substituted into equation 1.19 (equation 1.21).

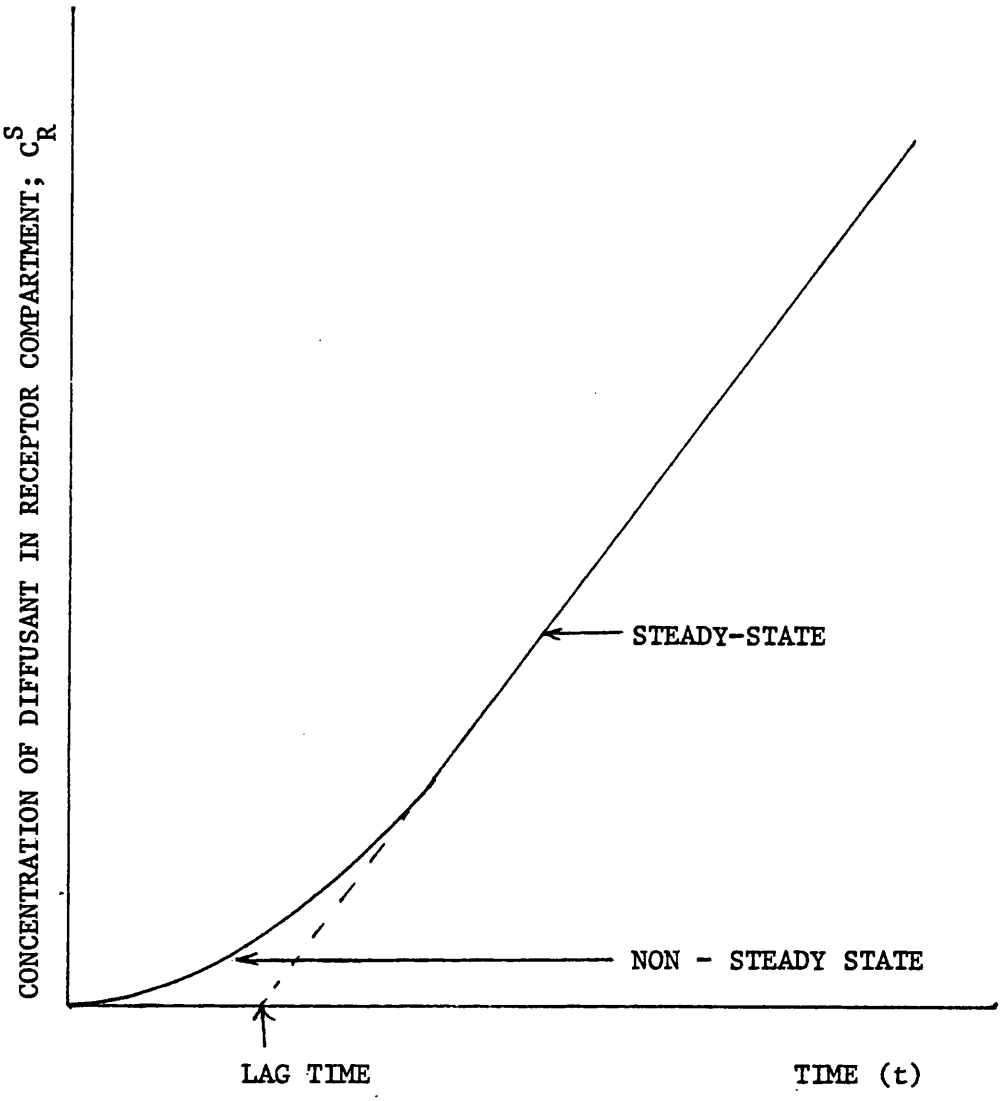


Figure 1.15 Schematic Representation of the Barrer Plot

$$\frac{dm}{dt} = \frac{\bar{D}.A.\ K.C_D^S}{\ell} \qquad \text{.....(1.21).}$$

The receptor phase concentration C_R^S may be obtained by introducing the receptor compartment volume (equation 1.22).

$$\frac{dC_1^S}{dt} = \frac{\bar{D}.A.K.C_D^S}{\ell \cdot V_R} \qquad \text{.....(1.22).}$$

In several practical systems the permeability of solute is represented by equation 1.23.

$$\frac{dC_R^S}{dt} = \frac{P.A.C_D^S}{\ell \cdot V_R} \qquad \text{.....(1.23).}$$

Under conditions where the isotherm is linear P and $\bar{D}$ can be calculated from the steady state slope of the Barrer Plot provided that the donor solution concentration is known together with the dimensions of the permeability apparatus. Comparison of equation 1.22 and 1.23 indicates that the permeability, sorption and diffusion processes are interelated by the expression given in equation 1.24

$$P = K.\bar{D}. \qquad (1.24)$$

1.6.1.2 The Characterisation of Diffusion Using Sorption Experiments

Values of $\bar{D}$ for polymeric sorbents may be obtained by measuring the rate of which the fractional approach to equilibrium takes place, Practically, the most convenient experimental system consists of a small volume of solution, into which the sorbent is placed. The progress of mass transfer into the solution is then monitored by the change in solute concentration as a function of time. The solution of Fick's equation (equation 1.15) for these systems is complicated by the boundary condition, which changes as a function of time due to the changing surface concentration. Several mathematical solutions, however, have been published for the condition where the amount of solute in solution and polymer remains constant as diffusion proceeds (Crank 1956). A solution to equation 1.15 obtained using the conservation of mass condition was proposed by Berthier (1952) who used it as a method of measuring self diffusion. The equation relating fractional uptake to the dimensionless parameter, T, representing time is given in equation 1.25

$$\frac{M_t^P}{M_\infty^P} = (1+\psi)\left\{1-\exp[T^2]\,(1-\frac{2}{\sqrt{\pi}}\int_0^T \exp[-T^2.dT])\right\} \quad .....(1.25)$$

where : M_t^P = the mass in the polymer after time, t.

M_∞^P = the mass in the polymer after infinite time (at equilibrium)

$$T = \frac{\bar{D}t}{\ell^2}$$

where : 1 = Half the thickness of a sorbent membrane

$$\psi = \left[\frac{M_o^S}{M_{eq}^P}\right] - 1\,0$$

Continued ...

where: M_0^S = the initial mass in solution

The solution of equation 1.15 expressed in equation 1.25 assumes that the sorbent is in the form of a membrane where sorption into the edges is negligable compared to sorption by the two faces. The Ψ term is a function of the sorption coefficient, K, as it is further assumed that the concentration of solute just within the surface is K times that in the solution (Crank 1956). Berthier (1952) published tables of M_t^P/M^P versus T for different values of T. thus enabling the construction of simulated uptake curves based on the functional form of equation 1.25.

The value of $\bar{D}$ can be calculated by a process refered to as curve matching (Tien and Thodos 1960). Comparison of M_t^P/M_{eq}^P against $t^{\frac{1}{2}}$ with the theoretical plot of M_t^P/M_{eq}^P versus T should reveal a functional similarity if the diffusion model is a satisfactory representation of the actual diffusion process. The experimental value of M_t^P/M_{eq}^P is read off for a selected $t^{\frac{1}{2}}$ and is then matched to the theoretical plot to obtain $\bar{D}t/\ell^2$. , from which $\bar{D}$ can be evaluated, as $t^{\frac{1}{2}}$ and ℓ are known. An alternative matching technique was proposed based on an observation that the experimental and theoretical curves are essentially linear up to $M_t^P/M_{eq}^P = 0.6$ (Kapadia et al 1964a). In this case $\bar{D}$ can be calculated from equation 1.26

$$\frac{\bar{D}}{\ell^2} = \frac{\text{Slope (experimental)}}{\text{Slope (theoretical)}} \quad \ldots\ldots\ldots\ldots (1.26)$$

The expressions given above are derived for sorbents in the form of films or membranes. Berthier has also published tables for spherical sorbents, in which radial diffusion replaces linear diffusion (Berthier 1952).

In both approaches to calculating $\bar{D}$, and for the calculation of P, the experimental conditions must parallel the boundary conditions of a particular published solution exactly. The sorbent matrix is considered to be homogeneous such that $\bar{D}$ is constant at all points within the matrix.

The values of the diffusion coefficient obtained by sorption and permeability experiments should not be directly compared as values for the same membrane, determined by the two methods, have been shown to disagree (Berg et al 1965). The various methods used to obtain $\bar{D}$ by experimentation will be subject to different types of error which will result in the numerical disagreement in diffusion coefficient data. Different solutions of equation 1.15 also make different simplifying assumptions which will also contribute to inconsistent numerical values of $\bar{D}$. For comparison, it is recommended that a particular experimental technique and solution to the diffusion equation are adopted as a standard procedure.

1.6.1.3 Factors Affecting the Dynamic Interaction of Solutes with Polymers.

The relationship between the sorption, permeability and diffusion processes are given in equation 1.26, the latter two being rate processes. The less fundamental permeability coefficient is sensitive to changes in the equilibrium sorption process which is not itself time dependent. The physicochemical factors affecting sorption will also affect permeability which have been discussed previously in Section 1.5.3

1.6.1.3.1 Temperature

The diffusion process is considered to occur by the transfer of solute molecules between free space in the matrix brought about either by thermally induced segmental motion of the polymer chains (Barrer 1951) or localised changes in density (Kummins and Kwei, cited in the Encyclopedia of Polymer Science). At higher temperatures the creation of free space will occur more rapidly thus facilitating the transfer of solute by either mechanism. An investigation of the effect of temperature on the diffusion of salicylic acid by a nylon polymer showed that the Arrhenius relationship could be applied to account for thermally induced changes in $\overline{D}$ (equation 1.27) (Kapadia et al 1964).

$$\log \overline{D} = \log \overline{D}_o - \triangle E/2.303R.T. \quad \ldots\ldots\ldots\ldots (1.27)$$

where : $\overline{D}_o$ = the diffusion coefficient at infinite temperature

R = the gas constant

$\triangle E$ = the activation energy for the diffusion process.

The effect of temperature on the permeability of solutes will be a complex function of its effects on the sorption and diffusion processes. Sorption is generally an exothermic process, the extent of which decreases as temperature increases. Although sorption processes will normally be characterised by a negative value of ΔH^0, endothermic sorption processes have also been reported (Ho 1977). The diffusion process is a rate process and as such is characterised by a positive activation energy as higher temperatures promote a higher rate of mass transfer. As permeability is the product of the sorption and diffusion processes, the effect of temperature on permeability will depend upon the numerical values of the enthalpy of sorption and the activation energy for diffusion (Bray 1977).

1.6.1.3.2 Polymer Structure.

Structural changes in polymers enhancing the degree of segmental mobility will also increase diffusion and decrease the value of $\bar{D}$. Alternatively changes which restrict movement will reduce diffusion. Earlier studies concerned with the diffusion and permeability of gases and vapours through plastics and rubbers have shown that an increase in density, crystallinity (Alter 1962, Meyers 1962) and cross-linking (Kumins, 1965) all decrease the rate of solute permeation. The molecular weight of the polymer is also important in some cases. Fites et al (1970) found that the lower molecular weight grades of poly (methyl vinylether)-maleic anhydride copolymer were more permeable to caffeine than higher ones.

The effect of temperature on the structure of polyamides has been discussed in Section 1.5.3.4. The different studies, present at different temperatures have been shown to influence the sorption of ethyl 4-aminobenzoate (Ho, 1977).

Studies investigating the permeation of ethyl 4-aminobenzoate through non-oriented films of nylon 6, 11 and 12 have shown that the amide frequency influences the diffusion and permeation processes. Decreasing the number of methylene groups, thus increasing the amide frequency, allows solute to diffuse more easily as methylene chains are known to produce crystallinity in the matrix (Ho 1977).

Orientation of the polymer chains has been shown to affect the transport properties of polyamides. Investigation of the sorption and diffusion of ethyl 4-aminobenzoate through non-oriented, monoaxially and biaxially oriented nylon 6 film showed that the permeation rate was higher in the non-oriented film (Ho 1977). This was attributed to the more open, random structure of the non-oriented form which would create an easier pathway for the diffusant.

1.6.1.3.3 Solute Structure.

The rate of diffusion and permeation of solutes of high molecular volume is generally lower for a given polymer than those with a relatively lower molecular volume. Rodell et al (1966) found that as the molecular size of a series of 4-hydroxybenzoates increased, the rate of diffusion and permeation in nylon decreased. The configuration of a substituent, and its effect on mass transport in nylon 6 has also been demonstrated using a series of hydroxybenzoic acid derivatives. The diffusion rate of 2-hydroxybenzoic acid was shown to be greater than the 3- and 4-substituted derivatives indicating that steric effects may alter relative rates of solute transport (Rodell et al 1966).

1.6.1.3.4 Polymer Additives.

Additives such as fillers and plasticizers are used in many

polymer formulations to modify the medicinal properties of the plastic material or its appearance. Fillers and plasticizers will also affect diffusion as segmental motion in the matrix is generally affected by the presence of these additives (Brydson 1970). Phthalate and citrate plasticizers have been shown to increase the diffusion of ethyl 4-aminobenzoate in P.V.C (Bray 1977). Conversely, fillers have been demonstrated to reduce the permeability of a silastomer polymer to 4-aminoacetophenone(Flynn and Roseman 1971) and silastic to ethyl 4-aminobenzoate (Most 1970).

1.6.2 Diffusion in Active Carbon Sorbents.

The limiting step in the rate of uptake of solutes by active carbon is generally considered to be the intrapore diffusion of solute. The approach which correctly characterises the diffusion properties of active carbon sorbents involves solution of equation 1.15 for an appropriate set of boundary conditions which will also determine the experimental design. Unlike polymeric sorbent systems, active carbon kinetics experiments are restricted to the sorption of solutes from well-stirred solutions of limited volume. The kinetics of mass transfer within active carbon sorbents has received little attention due to the complexity of relating the solution of equation 1.15 to a realistic model of the likely mechanism of sorption. Attempts have been made to obtain values of the diffusion coefficient for mass transfer in active carbon, these are discussed in the next section.

Several workers have selected the most mathematically convenient model solution to Fick's second law (equation 1.15) despite the practical difficulties encountered when trying to comply with the boundary conditions. When solute diffuses from a

solution, which remains at constant concentration throughout the determination, into a sorbent which is spherical and homogenous the diffusion coefficient can be calculated from equations 1.28 or 1.29 (Crank 1956).

$$\frac{M_t^c}{M_{eq}^c} = \frac{6(\bar{D}t)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}a^2} - \frac{3\bar{D}t^2}{a^2} \quad ; \quad \text{for } \frac{(\bar{D}t)^{\frac{1}{2}}}{a^2} \leq 0.4 \quad \ldots\ldots\ldots(1.28).$$

$$\frac{M_t^c}{M_{eq}^c} = 1 - \frac{6}{\pi^2} \text{ EXP } \frac{(-\pi^2\bar{D}.t)}{a^2} \quad ; \quad \text{for } \frac{(\bar{D}t)^{\frac{1}{2}}}{a^2} \geq 0.4 \quad \ldots\ldots\ldots(1.29).$$

where M_t^C = concentration per unit weight in the carbon at time t

M_{eq}^C = concentration per unit weight in the carbon at equilibrium

Equations of the type 1.28 and 1.29 have been used in studies of the kinetics of sorption from the gas phase. The constant concentration boundary condition is achieved by passing a stream of gas over the adsorbent, then weighing the adsorbent material on a microbalance to assess the uptake (Habgood 1958). This method is not strictly applicable to sorption from solution as solute uptake is estimated by the change in concentration of the solute in the solution (equation 1.1). This is clearly not satisfactory when equations 1.28 and 1.29 are only valid if the solution concentration remains constant. The diffusion coefficients of salicylic acid and hippuric acid in active carbon have been determined using a large volume of solution such that the concentration, although changing continuously, remained effectively constant (Dedrick et al 1967). Theoretical curves of the

fractional approach to equilibrium versus $\bar{D}t^{\frac{1}{2}}/a$ (where a is the equivalent sphere radius for the carbon granules) were produced using equations 1.28 or 1.29 and matched to experimentally determined plots, to obtain $\bar{D}$. The experimental observation that the plot of M_t^c/M_{cq}^c versus $t^{\frac{1}{2}}$ was linear up to a value of 0.6 indicated that equation 1.28 could be used. Parkash (1974) obtained $\bar{D}$ values for the sorption of Paraquat and Diquat onto active carbon using a modified equation 1.28 (equation 1.30).

$$\bar{D} = \pi \left[\frac{V}{2A} \cdot \frac{1}{M_{eq}^c} \cdot \frac{dm_t^c}{dt^{\frac{1}{2}}} \right]^2 \quad \text{.....(1.30).}$$

where $V = \frac{4}{3} \pi a^3$ = the sphere volume.

$A = 4 \pi a^2$ = the sphere surface area

$\frac{dm^c}{dt^{\frac{1}{2}}}$ = the slope of the linear region of the transformed kinetic profile

Parkash determined the sorption kinetic profile from limited volume, apparently making no attempt to comply with the constraints of the boundary conditions implicit in the use of equation 1.30. Although a linear plot of uptake versus $t^{\frac{1}{2}}$ was obtained it is not clear whether the values of $\bar{D}$ obtained from this study are valid.

The experimental observation that the solute uptake when plotted as a function of $t^{\frac{1}{2}}$ gives rise to a linear plot has been used to characterise sorption rates. Weber and Morris (1963) defined a relative rate constant as the slope of the intial linear region of the uptake versus $t^{\frac{1}{2}}$ plot. They did not attempt to calculate $\bar{D}$ but used the sorption rate constant as a relative estimate of the initial rates of sorption of various solutes under different initial conditions. These workers emphasised that the relative rate constant is only an empirical estimate of relative rates when

a standard apparatus is used in its determination. Furthermore, the value of the rate constant is a function of the dimensions of the apparatus as well as the mass transfer characteristics of the sorbent.

The experimental procedures developed to solve Fick's second law are clearly unsatisfactory for the reasons stated. Sorption from a limited volume of solution which contains a finite amount of solute will be characterised by a time-dependent boundary condition as the concentration of solute decreases and sorption proceeds. A method of solution which incorporates a time-dependent boundary condition will be a more precise representation of the actual sorption process. The sorption of solutes by active carbon generally gives rise to non-linear L type isotherms which further complicates the solution to equation 1.15. In many cases it is convenient but incorrect to assume that the uptake of solute is a linear function of the equilibrium concentration i.e. that sorption is described by a C type isotherm. It is, therefore, important that a solution to equation 1.15 incorporates expressions which ensure that L type isotherm behaviour is taken into consideration. Two solutions to equation 1.15 include a time-dependent boundary condition with non-linear isotherm behaviour which can be used to evaluate the experimental data obtained from finite, limited volume conditions. These solutions proposed by Tien and Thodos (1960) and Weber and Rumer (1965) are discussed in the next section.

A solution to equation 1.15 has been derived where the mass of solute at the surface of the sphere is a known function of time (Crank 1956). The concentration gradient between the surface of the "spherical" sorbent and its centre which is initially zero,

continually changes as a function of time as solute is taken up. The mass at the surface can be determined as a function of time if the bulk phase solution concentration is known and the isotherm constants are available. This subsurface mass of solute is related to time by a virial equation of the form shown in equation 1.31 which is used as a time-dependent boundary condition in the solution of equation 1.15 (Tien and Thodos 1960).

$$M^{C}_{t(subsurface)} = A + Bt + Ct^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.31).$$

$M^{C}_{t(subsurface)}$ = mass of solute sorbed at the subsurface corresponding to the bulk concentration at time, t.

A. B. C = Virial coefficients.

The final relationship, employing equation 1.31, for use to calculate the theoretical curve for matching to the experimental data is given in equation 1.32.

$$\frac{M^{c}_{t}}{M^{c}_{t(subsurface)}} = 1.0 - \left\{ \frac{6\xi}{\pi^2} \phi_1 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2\pi^2}{\xi}\right) + \phi_2 \left[\frac{\xi}{15} - \frac{6}{\pi^4}\xi \sum_{n=1}^{\infty} \frac{1}{n^4} \exp\frac{(-n^2\pi^2)}{\xi} \right] \right.$$

$$\left. + \phi_3 \left[\frac{2\xi}{15} - \frac{12\xi^2}{945} + \frac{12\xi^2}{\pi^6} \sum_{n=1}^{\infty} \frac{1}{n^6} \exp\frac{(-n^2\pi^2)}{\xi} \right] \right\} \ldots\ldots\ldots (1.32).$$

Continued.....

Continued

where M^C_t = mass of solute sorbed at time t.

M^C_t = mass of solute sorbed at the subsurface corresponding to the t(subsurface) both concentration at time t.

$\phi_1 = A / A + Bt + Ct^2$

$\phi_2 = Bt / A + Bt + Ct^2$

$\phi_3 = Ct^2 / A + Bt + Ct^2$

$\xi = a^2 / \bar{D}t$

The curve matching procedure involves plotting $M^C_t / M^C_{t(subsurface)}$ as a function of time from equation 1.26 for arbitrary values of ξ. At this point where the experimental and theoretical curves intersect $\bar{D}$ can be calculated from equation 1.33

$$\xi = \frac{a^2}{\bar{D} \cdot t_{(intersection)}} \qquad \text{.....(1.33)}$$

As ξ is arbitrarily set, a is known and the intersection time is obtained by curve matching, $\bar{D}$ can then be solved as the remaining unknown. Meier (1972) obtained values of $\bar{D}$ in the range 1.2×10^{-11} m^2 sec^{-1} (t-butanol) to 1.9×10^{-14} m^2 sec^{-1} (vitamin B_{12}) for the sorption of solutes of varying molecular weight by active carbon. The $\bar{D}$ value for the sorption of phenol by active carbon using this method was reported to be 6.9×10^{-12} m^2 sec^{-1} (Miller and Clump 1970).

The previous models for intrasorbent diffusion have assumed that the "spherical" sorbent is homogeneous and that all of the solute present in the granule is free to diffuse. These models have appeared to neglect the high activity of carbon and the possibility that significant quantities of solute may be adsorbed from the lumen of pores on to the pore wall (Weber and Rumer 1965). They proposed the pore diffusion model for sorption where solute taken up by the sorbent is subdivided into free solute and immobilised solute. The model attempts to obtain $\bar{D}$ by solution of Fick's equation with an added term to account for immobilised solute (equation 1.34).

$$\frac{dc_t^C}{dt} = \bar{D}.\frac{d}{dx}\left(\frac{dc_t^C}{dx}\right) - \frac{dM_t^C}{dt} \qquad \text{.....(1.34)}$$

The complexity of equation 1.34 especially if the sorption isotherm is nonlinear, prohibits a solution by calculus (a so-called analytical solution). The solution of equation 1.34 is obtained by the method of finite differences (Crank 1956) which is explained in detail in appendix 3. The principle of the solution involves sub-dividing the sphere into a number of concentric shells across which the concentration gradient is linear. Finite difference equations are used in place of the differentials in equation 1.34 such that the concentration of solute of each shell:shell interface is obtainable as a function of time and radial distance into the sphere. The sorption isotherm is used to calculate the amount of solute at the shell:shell interface which is free and bound. As the

calculation proceeds, material is balanced between the sphere and the surrounding solution such that as time proceeds, solute is incrementally depleted from solution. The calculation procedure produces a theoretical curve of percentage residual initial concentration versus $\bar{D}t/a^2$, which can be matched to experimental data to obtain $\bar{D}$. Weber and Rumer succeeded in accurately predicting the shape of the sorption rate profile for a series of alkyl benzenesulphonate derivatives. The $\bar{D}$ values reported were of the order $10^{-10} - 10^{-11}$ m^2 sec^{-1} which are approximately four orders of magnitude higher than those calculated by the homogeneous sphere model.

1.6.2.1 Factors Affecting the Dynamic Sorption of Solutes by Active Carbon.

The factors affecting the dynamic sorption of solutes by active carbon are similar to those for sorption in polymers as the diffusion process is fundamental to the nature of mass transport in both sorbents. The relative sorption rate constant is an empirical parameter and, as such, is dependent upon the nature of the mass transport characteristics of the sorbent and the dimensions of the experimental system. The diffusion coefficient is, however, a more fundamental parameter and for any given solute at a given temperature is a function of the mass transport properties of the sorbent alone.

1.6.2.1.1 Temperature.

The rate of sorption by active carbon increases as temperature increases. Both the relative rate constant and the diffusion coefficient parameters are temperature dependent and can be related to temperature using the Arrhenius relationship (equation 1.28). The

Arrhenius plot can be used to obtain an activation energy for the diffusion process. A value of 15 KJ mol^{-1} was obtained for the sorption of 3-dodecyl benzenesulphonate by active carbon using rate constant data (Weber and Morris 1963) and 20 KJ mol^{-1} and 28 KJ mol^{-1} were obtained for Diquat and Paraquat, respectively, on active carbon using diffusion coefficient data (Parkash 1974).

1.6.2.1.2 Experimental Conditions.

The stirring rate was shown to influence the rate of adsorption of 3-dodecyl benzenesulphonate by active carbon below 500 rpm (Weber and Morris 1963). This effect was attributed to the contribution to overall diffusion of the static boundary layer which is higher at low stirring rates but is eliminated at high stirring rates. The rate of sorption was found to increase in proportion to the square-root of the initial solute concentration. The slopes of the percentage residual initial concentration versus time profile were greater for dilute solutions than for more concentrated ones, although the overall mass of solute removed was less (Weber and Morris 1963). A later study calculating $\bar{D}$ by the method of finite differences (Appendix 3) demonstrated that, provided the effect of film diffusion was eliminated at high stirring rate, the diffusion coefficient was virtually independent of experimental conditions (Weber and Rumer 1965).

1.6.2.1.3 Solute Structure.

As with the polymer systems, an increase in molecular volume of the solute decreases the rate of sorption. Weber and Morris (1963), demonstrated that as the chain length of the alkyl substituent in a

series of alkyl benzenesulphonates increased, the rate of sorption, represented by the rate constant, decreased. A steric effect was also shown to be important as different substitution patterns for molecules of the same molecular weight affected the rate of solute transfer. The molecular size effect was also apparent when $\bar{D}$ values were used to represent the rate of sorption (Weber and Rumer 1965).

1.6.2.1.4 Sorbent Structure.

The activation process influences the nature of the internal pore network which in turn affects the rate of sorption. The uptake of Paraquat by various active carbons has been shown to be influenced by the different pore networks arising from different conditions of activation (Parkash 1974). Two samples of an active carbon were used with B.E.T. surface areas of 660 and 1280 $m^2 g^{-1}$. As the surface area was increased the rate constant for the sorption of Paraquat increased from 3.3 to 7.1 x 10^{-3} $\mu mol g^{-1}$ hr^{-1} respectively. The increase in the rate of sorption was clearly affected by the degree of activation, however, no mechanism was proposed to account for these findings.

The diffusion coefficients for a range of solutes of various molecular volume have been shown to correlate with the diffusion coefficients in water (Weber and Rumer 1965, Meier et al 1972). In this case the carbon pores would not affect the rate of mass transfer and, provided that the pore sizes were greater than the molecular volume of the diffusing solute, the sorption process would be expected to be independent of the nature of the activation process. The findings of Parkash, Weber et al and Meier et al would therefore appear to be conflicting.

1.6.2.1.5 pH.

The effect of pH has been shown to influence the rate of sorption for strong and weak organic electrolytes over a much greater range than the solute pka ± 2 pH units (Weber and Morris 1963). The effect was attributed to complex ionisation states involving both the solute and acidic and basic groups on the carbon surface.

1.7 SORPTION FROM DILUTE BINARY SOLUTE SOLUTION.

The study of solute sorption from dilute solution is concerned with the measurement of the uptake, or surface excess of the solute, excluding the sorption of the second component in the solution, the solvent. The addition of a third component may affect this system in several ways which are likely to be manifest in a change in the sorption characteristics of the original solute. Firstly, the second species (component 2) may act as a cosolvent for the first or original solute (component 1), thus increasing the solute-solvent/cosolvent interaction and reducing the overall extent of sorption. Secondly, component 2 may be taken up by the sorbent simultaneously with component 1 and competition may arise between them for common and limited adsorption sites. Again, this will result in a lowering of uptake of component 1, component 2 or both. Thirdly, component 2 may interact with component 1 forming a stable complex which has a completely different sorption profile to each of the individual solutes. This will result in an altered sorption profile for each of the components. Lastly, and particularly in the case of polymeric sorbents, component 2 in the system may act as a plasticizer, altering the physical structure of the matrix and in so doing, affecting the sorption profile of component 1.

1.7.1 The Sorption of Solutes from Binary Solute Solutions by Polymers.

The addition of ethanol and polyethyleneglycol (PEG) 400 to a solution of ethyl 4-aminobenzoate was shown to reduce the sorption of ethyl 4-aminbenzoate by nylon 6 (Richardson 1973). The extent of sorption decreased as the concentration of ethanol and (PEG) 400 increased, and this effect was attributed to these two solutes acting as cosolvents for ethyl 4-aminobenzoate. The Van't Hoff isochores for the sorption of ethyl 4-aminobenzoate in the presence of ethanol did not possess the characteristic point of inflexion associated with secondary phase transitions in the polymer. It was, therefore, suggested that ethanol could also act as a plasticizer for nylon 6. Similar findings have been reported for the cosolvent effect of ethanol and acetone on the sorption of mono and di-hydric phenols by a nylon polymer from aqueous solution (Belyaeva and Bykova, 1975).

The permeation of nylon films by quaternary ammonium compounds have been shown to be enhanced by the cosorption of the perchlorate ion (Agren et al 1974). Perchlorate ions are known to form ion pairs with quaternary ammonium compounds and the sorption of the neutral ion-pair complex would appear to be favoured. Sorption of the salicy late ion in the form of an ion-pair complex has similarly been demonstrated.

Competitive sorption processes have been reported for the colouring of nylon fibres by acid dyes (Encyclopaedia of Polymer Science and Technology). This phenomenon is exploited commercially in the dyeing unit-process known as levelling where a more uniform distribution of the acid dye is achieved in the plastic by the

addition of large colourless surfactant ions. As the dye is taken up by the plastic material it encounters competition from the colourless surfactant and consequently the rate of dye-bath exhaustion is lowered with a consequent improvement in colour uniformity. This process is only applicable to the dyeing of plastics where the dye-polymer interaction is due to an ion exchange mechanism

1.7.2 The Sorption of Solutes from Binary Solute Solution by Active Carbon.

Due to the high activity of active carbon and its affinity for a wide range of solutes, most of the binary solute systems studied have given rise to competitive sorption or replacement adsorption interactions.

Earlier studies have indicated that competition for adsorption sites was the probable mechanism (Kolthoff and Van der Groot 1929). Surface tension experiments at the air-solution interface showed that the surface tension of phenol was unaffected by the presence of hydroquinol or resorcinol. Both hydroquinol and resorcinol were, however, able to reduce the uptake of phenol on active carbon. Further studies showed that the reduction in adsorption of one solute in the presence of a preferentially adsorbed competitor was a relative effect and depended upon the sorption characteristics of both species. This was demonstrated by the displacement of hydroquinol by paracresol, and the displacement of lactose by phenol. The general principles of the competitive sorption process were confirmed by studies of the sorption of weak aliphatic and aromatic acids by active carbon (Ockrent 1932). In all cases the more strongly adsorbed species was preferentially adsorbed as shown by

the displacement of acetic, formic and trichloracetic acids by benzoic and salicylic acid.

The isotherms were all L type in nature and remained so in the presence of a competing species. Although the sorption of each species was lowered in competitive systems the overall total uptake did not exceed the total uptake predicted from non-competitive isotherms for the single solute sorption. Ockrent (1932), consequently modified the Langmuir equation to account for the sorption of solutes from binary solute solution based on single solute isotherm paramters. The modified Langmuir equations for sorption from binary solute mixtures are given in equations 1.35 and 1.36.

$$n_1 = \frac{n_{max.1}\, b_1' \, C_{eq1}}{1 + b_1' C_{eq1} + b_2' C_{eq2}} \qquad \text{.....(1.35)}$$

$$n_2 = \frac{n_{max.2}\, b_2' \, C_{eq2}}{1 + b_2' C_{eq2} + b_1' C_{eq1}} \qquad \text{.....(1.36)}$$

where all symbols follow from equation 1.3 and subscripts 1 and 2 refer to solute species 1 and 2 respectively.

Ockrent developed these equations by assuming that $n_{max.1} = n_{max\ 2}$, a statement which implies that both solutes adsorb onto the same surface which is composed of energetically homogenous sites.

If this is the case equation 1.37 follows from equations 1.35 and 1.36 and a plot of n_1/n_2 versus C_{eq1}/C_{eq2} should be linear. If the two single solute Langmuir equations and those of the mixed system are consistent the slope of this linear plot b_1'/b_2' should equal the same fraction obtained from single solute values of b_1' and b_2'. Systematic deviations between b_1'/b_2' calculated from the mixture and the two single solute systems were evident suggesting

$$\frac{n_1}{n_2} = \frac{b_1'}{b_2'} \cdot \frac{C_{eq1}}{C_{eq2}} \qquad \text{.....(1.37)}$$

that $n_{max.1}$ and $n_{max.2}$ were not equal and that the two single solute and the binary solute equations were not consistent, although the plot was linear. This study was used as a basis for an investigation of the sorption of phenol, benzene sulphonate and nitrobenzene from binary solute solution by active carbon (Weber and Morris 1964). The relative competitiveness of each solute was shown to be a function of the relative affinity and concentration of the solutes which are related by the Langmuir equation. The study also demonstrated that the total amount of solute adsorbed from the mixtures exceeded the saturation uptakes of either species as determined from single solute sorption, although good agreement was obtained using equations 1.35 and 1.36 with single solute b' and n_{max} values. It was suggested

that the sorption surface for each component was not the same and that competitive sorption could only take place on the area of surface common to both solutes. Equations 1.30 and 1.31 were modified to account for this proposed common area effect by adjusting the n_{max} term (Jain and Snoeyink 1973). Using similar solutes to Weber and Morris, the competitive sorption effect was confirmed. It was assumed that the excess area for sorption is given by equation 1.38.

$$n_{exclusive.1} = n_{max.1} - n_{max\ 2.}$$

$$\text{where } n_{max\ 1} > n_{max\ 2} \qquad \text{.....(1.38)}$$

Equation 1.35 was then modified to relate uptake to the amount of sorption taking place on the common and exclusive areas giving rise to equation 1.39.

$$n_1 = \frac{n_{exclusive.1}\, b_1' C_{eq1}}{1 + b_1' C_{eq1}} + \frac{n_{max.2}\, b_1' C_{eq1}}{1 + b_1' C_{eq1} + b_2' C_{eq2}} \qquad (1.39)$$

Equation 1.39 was then used in conjunction with equation 1.36 to predict competitive sorption based on b' and n_{max} parameters determined from single solute isotherms.

The uptake of solutes was successfully predicted using single solute Langmuir isotherm constants and by applying combinations of equations 1.35 and 1.36 or equations 1.39 and 1.36 as the n_{max} terms of both solutes were, coincidentally, similar. This calculation procedure was not capable of predicting solute uptake when one or other species was taken up in the ionised form.

The sorption of phenol, 4-nitrophenol and para-cresol by active carbon from binary solute solution has also been described using a mixed Langmuir equation of the type given in equation 1.35 modified to account for behaviour on a hetrogeneous surface (Okasaki et al 1980). The homogeneous predictive models equate the single solute isotherms by eliminating the n_{max} term using the Langmuir model assumption that the available surface area is a function of the sorbent and not the adsorptive characteristics of the solutes. In this case, "competitiveness" of each solute is a function of affinity, represented by the b' parameter which is itself a function of adsorption energy, and the equilibrium concentration. The heterogeneous surface model, however, fixes the value of maximum uptake and solves an equation of the type given in equation 1.35 for the sorption onto a finite number of sites of similar energy. In this method, the single solute isotherm functions are equated by fixing the energy relationship term as well as the maximum uptake term such that competitiveness is a function of relative concentration only.

Radke and Prausnitz (1972b) developed a method of predicting binary solute equilibria based on the Gibb's isotherm. This method is

particularly useful when single solute data cannot be fitted to the Langmuir equation which is an important pre-requisite to the use of equations 1.36, 1.37 and other relationships associated with the mixed Langmuir procedure. Unlike the isotherm relationships described previously, the Gibbs adsorption isotherm gives uptake as a function of concentration and a third parameter, the interfacial tension (equation 1.40).

$$-\Gamma = \frac{A\,C_{eq}}{R.T} \cdot \frac{d\gamma}{d\,C_{eq}} \qquad \text{.....(1.40)}$$

where γ = interfacial tension

A = the surface area of the interface

Γ = the surface excess concentration which $\propto$ n : the uptake in mol Kg^{-1}

The procedure developed by Radke assumes that when the interfacial tension of the single solute systems and the mixture are equal, the binary solute uptake can be determined from application of ideal solution theory and single solute isotherm data. It is necessary to obtain the interfacial tension of the single solute isotherm data and a rearrangement of equation 1.40 (equation 1.41) as interfacial tension cannot be directly measured at the solid-liquid interface.

$$-\frac{A\gamma}{RT} = \int_{C_{eq}=0}^{C_{eq}} \frac{n^1}{C_{eq}} . dC_{eq} \qquad \text{.....(1.41).}$$

where n^1 = the equilibrium uptake corresponding to the equilibrium concentration C_{eq}.

The theoretical application of ideal solution thermodynamics to binary solute sorption is clearly outlined in Radke's paper, the calculation procedure only will therefore be summarised here.

1) Using equation 1.41 and the single solute isotherms obtain

$$-\gamma_1 = f_1 (C_1^o) \qquad \text{.....(1.42a)}$$

and

$$-\gamma_2 = f_2 (C_1^o) \qquad \text{.....(1.42b).}$$

where C_1^o = single solute equilibrium concentration of solute 1.

C_1^o = single solute equilibrium concentration of solute 2.

2) It has been shown that for the mixture, at constant interfacial tension

$$C_1 = C_1^o Z_1 \qquad \text{.....(1.42c)}$$

$$C_2 = C_2^o (1 - Z_1) \qquad \text{.....(1.42d)}$$

where C_1 = equilibrium concentration of solute 1 in mixture

C_2 = equilibrium concentration of solute 2 in mixture

Z_1 = adsorbed phase mole fraction of solute 1

3) As the mixture and the single solute systems are at the same interfacial tension, equations 1.42c and 1.42d can be substituted into equations 1.42a and 1.42b respectively to give:

$$f_1 \left(\frac{C_1}{Z_1} \right) - f_2 \left(\frac{C_2}{1 - Z_1} \right) = 0 \quad \text{.....(1.42e)}$$

which is solved by trial-and-error to obtain Z_1.

4) Knowing Z_1 (and given the concentrations of solute 1 and 2 in the mixture), the single solute equilibrium concentrations at the same interfacial tension can be derived from equations 1.42c and d.

5) Knowing C_1^o and C_2^o, obtain n_1^o and n_2^o the single solute uptakes for solutes 1 and 2 respectively using single solute isotherms

6) The following expression has been derived to calculate the total adsorption, N^T, in the mixture from single solute data at a given interfacial tension

$$\frac{1}{N^T} = \frac{Z_1}{n_1^o} + \frac{(1 - Z_1)}{n_2^o} \quad \text{.....(1.42f)}$$

7) The equilibrium uptake for the individual solutes in the adsorbed phase n_1 and n_2 can be derived as follows

$$n_1 = N^T . Z_1 \quad \text{.....(1.42g)}$$

$$n_2 = N^T . (1-Z_1) \quad \text{.....(1.42h)}$$

The calculation procedure is straightforward with the exception of step 3, the calculation of Z_1, which is of fundamental importance to the calculation. This stage is solved by an iteration method of trial-and-error using a computer. This calculation procedure has been used in several independent studies and has successfully predicted a wide range of multisolute equilibrium systems. Radke and Prausnitz (1972b) have shown, however, that the prediction of systems with high total uptake is poor due to activity effects in the adsorbed phase. Jossens et al (1978) have used the procedure successfully to account for the behaviour of phenol:4-nitrophenol systems and 4-chlorophenol:4-nitrophenol uptake by active carbon. The method was less applicable to 4-nitrophenol:benzoic acid and 4-chlorophenol: phenylacetic acid systems where the solute was adsorbed in the ionised form in each system. The calculation procedure has also been successfully applied to phenol: aliphatic acid mixtures (Misic and Suzuki 1975) and phenol: 4-nitrophenol and p-cresol: 4-nitrophenol systems (Okazaki et al 1980).
The models of sorption from binary solute solution discussed above have attempted to develop predictive schemes for the equilibria of the two participating solutes based on the data of two single solute isotherm equations. The competitiveness of each solute is, therefore, obtained from a knowledge of the single solute sorption,

and the resulting equilibria can be predicted without prior knowledge of the competitive sorption equilibria. Fritz and Schluender (1974) proposed a purely empirical approach to the prediction of binary solute sorption based on the development of a multiparameter expression which was fitted to experimental binary sorption data. A study of the sorption of phenol and 4-nitrophenol from binary solute solution showed that the sorption isotherms of both solutes were L_2 type and that a high degree of suppression was observed for phenol, whereas, 4-nitrophenol was virtually unaffected. Using a general equation (equation 1.43) and binary solute experimental data, the various constants were obtained by graphical procedures.

$$n_1 = \frac{a_{10}[C_{eq1}]^{b_{10}}}{\chi_1 + a_{11}[C_{eq1}]^{b_{11}} + a_{12}[C_{eq2}]^{b_{12}}} \quad \text{.....1.43}$$

where n_1 = equilibrium uptake of solute 1 per unit weight of sorbent

C_{eq1} = equilibrium concentration of solute 1

C_{eq} = equilibrium concentration of solute 2

χ_1 = empirical constant usually equal to 1.0 or zero

a_{10}, b_{10} = empirical constants from single solute isotherm data.

a_{11}, b_{11}, a_{12}, b_{12}, = empirical constants from binary solute isotherm data.

(The second solute will have a similar equation).

The similarity between equation 1.43 and equation 1.35 is marked.

Fritz and Schluender however, use both experimental binary and single solute data to obtain their constants, whereas equation 1.35 is derived totally from single solute data. The final empirical expressions for 4-nitrophenol (solute 1) and phenol (solute 2) are given in equation 1.44 and 1.45, respectively.

$$n_1 = \frac{3.25\, C_{eq1}^{1.31}}{C_{eq1} + 0.0185\, C_{eq}^{1.20}} \quad \text{.....1.44}$$

$$n_2 = \frac{2.16\, C_{eq}}{C_{eq1}^{0.77} + 14.0\, C_{eq2}^{0.70}} \quad \text{..... (1.45)}$$

Equations 1.44 and 1.45 were shown to agree closely with the experimental data.

1.8 DYNAMIC SORPTION FROM BINARY SOLUTE SOLUTIONS.

A survey of the chemical and pharmaceutical literature reveals that there has been no investigation of the rate of sorption of solutes from binary mixed aqueous solutions by polymers. However, considerable interest has been shown in the apparent loss of sorbent efficiency of active carbon in binary solute systems with respect to rates of solute uptake, by the civil, chemical and biomedical engineering disciplines. These investigations are reviewed below.

1.8.1 THE DYNAMIC SORPTION OF SOLUTES FROM BINARY MIXED SOLUTION BY ACTIVE CARBON

Preliminary studies investigating the rates of uptake of phenol derivatives and surfactants by active carbon have shown that a mutual suppression of uptake rate takes place in binary solute systems (Weber and Morris 1964b). The surfactant molecules were shown to suppress the rate of uptake of the phenolic derivatives to a much higher extent than they themselves were affected. It was suggested that the mechanism of rate suppression was congestion of the lumen of the porous channels where steric effects reduced the rate of mass flow. Although the sorption rate of each solute was suppressed, the overall total mass transfer of both solutes was greater than the rate of either solute from single solute systems. The general findings of this study were confirmed by an investigation of the rate of sorption of phenolic and fatty acid derivatives (Huang and Steffens 1976). As the homologeous series of fatty acids ascended from acetic to octanoic, the rate of sorption increased. The rate of sorption of the phenolic derivatives increased as follows: phenol, 2-aminophenol, benzene 1:2 diol and benzene 1:3 diol. It was suggested that the rank order of uptake for the fatty acid derivatives could be predicted from solubility considerations, whereas the rank order of the phenolic derivatives appeared to be a function of both solubility and molecular size. In all cases the phenolic derivatives suppressed the rate of sorption of the fatty acids to a much higher extent than they themselves were influenced. In contrast to the previous study by Weber and Morris (1964b), the major factor influencing rate suppression was thought to be competitive adsorption as opposed to pore congestion. The sorption rate profile for the

low affinity solute showed the presence of a minimum suggesting that displacement of solute could be occurring The presence of a minimum in the rate profile of phenol in the binary mixed solution with 4-nitrophenol has also been demonstrated (Fritz et al 1978). The sorption rate profile for the uptake of 4-nitrophenol in the binary system was unaffected by phenol in contrast to that for phenol which showed a high degree of suppression was taking place. The effect of molecular size on the competitive sorption kinetics of model solutes with molecular weights ranging from 113 (creatinine) to 500 (inulin) has been studied (Gundermann and Lie 1978). The rate of sorption of creatinine was not significantly affected by any solute regardless of molecular size but the rate of sorption of bromsulphthalein (molecular weight 774) was reduced in the presence of inulin. It was concluded that the rate of sorption of low molecular weight solutes was unaffected by cosorption of other species, but, middle and high molecular weight solutes were affected. Single solute rate data and sorption isotherm data was not given and no mechanism for these findings was proposed although a differential molecular sieve mechanism would appear to be a likely explanation.

In all cases, no quantitative description of binary solute rate data was attempted and the sorption rate profiles for the various solutes were compared visually to account for the kinetic behaviour of the binary systems.

1.9 SORPTION OF SOLUTES BY POLYMER COATED ACTIVE CARBON

Polymeric coatings were originally applied to the surface of active carbon used in haemopofusion to improve the biocompatibility of the carbon sorbents and to reduce the shedding of fine particles

(Hagstamm 1966). Several studies have shown that the mass transfer characteristics of the polymer coat can affect the sorption characteristics of the active carbon.

1.9.1 Method of Application of the Coat

The method of application of the coat will affect its integrity if the coating is complete; the permeability characteristics of the polymer will significantly influence the mass transfer characteristics of the overall sorbent. If, however, the degree of coverage is low due to an inefficient coating procedure, a biphasic interaction will arise where solute can interact with the carbon directly and also via the polymer covered areas of the surface (Meier 1972). Phase separation microencapsulation of active carbon using cellulose and nitrocellulose has been shown to result in coatings that are largely perforated with pinholes. An investigation of the sorption properties of the composite sorbent indicated that the polymer modifies the properties of the active carbon, however, a prediction of the change of properties due to the coat could not be made on the basis of polymer diffusion or permeability studies. It was concluded that some direct interaction was possible via the pinholes. A comparative study of the application of a polyhydroxyethyl methacrylate (poly HEMA) coat by spraying and impregnation on the uptake of paracetamol demonstrated that differences in mass transfer properties occur due to the application method. Impregnation resulted in the production of an incomplete coat which permitted greater solute access to the carbon than a fully complete sprayed coating (Gazzard and Langley 1974).

The method of application has also been shown to affect sorption capacity. The capacity of active carbon for a series of model

solutes of various molecular weight over the range of 113 to 1355 was reduced by 20 to 40 percent after application of a nitro - cellulose coat by phase separation microencapsulation (Meier et al 1972). In contrast, the capacity for paracetamol after coating with poly HEMA by spraying or impregnation was unchanged (Gazzard and Langley 1974). A similar study for the sorption of a wide range of therapeutic poisons by active carbon coated with poly HEMA by spraying has demonstrated that sorption capacity is unchanged (Kolthammer 1975).

Several studies have shown that the rate of uptake of solute decreases, in all cases, after application of a polymer coat, and that the rate of sorption decreases as coating thickness increases. (Kolthammer 1975, Skalsky and Farrell 1979, Gazzard and Langley 1974).

1.9.2 The Influence of Solute-Polymer Coat Interaction.

The ability of polymeric coats to control the rate of sorption of solutes by selective permeability has been demonstrated in several studies. The uptake of a series of hydrophilic and hydrophobic solutes by active carbon has been modified by applying polymer coats of varying hydrophobicity (Meier et al 1972). A nitrocellulose coat was applied which was then progressively denitrated thus producing a range of partially denitrated membranes. Hydrophobic species were found to be preferentially taken up by nitrocellulose coated active carbon and hydrophobic solutes by cellulose coated carbon.

The selective uptake of charged species by polymers possessing ionisable functional groups has been demonstrated for the sorption

of creatinine and uric acid in the presence of fatty acids (Huang 1974). The study showed that various copolymers of acrylic acid, cellulose and styrene selectively adsorbed creatinine in the presence of the lipid competitors enhancing its rate and extent of uptake compared to uptake on the uncoated carbon.

SECTIONS 2 and 3

EXPERIMENTAL

MATERIALS and METHODS

2.1 INSTRUMENTATION

2.1.1 pH Meter - A Radiometer type 27 pH meter fitted with a PHA 925a scale expander and a Pye Unicam model 291 expanded scale pH meter were used fitted with a Pye Unicam Ingold 401 glass-silver : silver chloride combined electrode. Both pH meters were internally compensated for temperature.

2.1.2 Spectrophotometers - Absorbance measurements were determined using a Pye Unicam SP 1800 double beam scanning spectrophotometer fitted with a Pye Unicam AR25 chart recorder, or a Unicam SP 500 single beam spectrophotometer.

2.1.3 Balances - An Oertling model R20 single pan analytical balance was used for weights in excess of 0.1g. Below 0.1g a Stanton Instruments Unimatic HCL5D single pan analytical balance was used.

2.1.4 Constant Temperature Baths - Three types of constant temperature baths were used.

a) A Grant SS30, thermostatted shaking water bath maintaining a constant temperature ± 0.1^{o} was used where agitation under isothermal conditions was necessary.

b) Grant SU6 water bath heaters capable of maintaining constant temperature ± 0.1^{o} were used to control the temperature of water baths for general purposes

c) A Laboratory Thermal Equipment Ltd viscometer bath fitted with a mercury contact thermometer capable of maintaining a constant bath temperature ± 0.005^{o} was used for dilute solution viscometry.

2.1.5 Melting Point Apparatus - Was supplied by Gallenkamp Ltd.

2.1.6 Mercury Porosimeter - A Carlo Erba model 1520 mercury porosimeter was used to determine the volume and distribution of pores in adsorbent materials with radii between 50 - 75,000 Å .

2.1.7 Microcalorimeter - Heats of wetting data were obtained by courtesy of the Physical Protection Division of the Chemical Defence Establishment (Porton Down) using a recording microcalorimeter (Maggs 1960).

2.1.8 Helium Air Pycnometer - A Micromeritics Corporation model 1302 Helium Air Pycnometer was used to determine true densities of powdered materials.

2.1.9 Micrometer - A Moore and Wright Ltd electronic hand micrometer was used to determine membrane thickness to a precision of $\pm$ 1.0 μm.

2.2 PHYSICAL MEASUREMENTS

2.2.1 pH Measurement - Solutions under test and standard buffers were equilibrated to the required experimental temperature prior to pH measurement or pH meter standardisation. pH meters were calibrated, in the expanded scale mode, before use, with two standard buffers at the upper and lower limit of the pH range over which determinations were being made. Standard buffers were prepared and stored according to the method described by Perrin and Dempsey (1974).

2.2.2 Temperature Measurement - Water bath temperatures were measured using mercury bulb thermometers calibrated in divisions of 0.1^{o}. Throughout this study all temperature measurements were made with reference to a calibrated mercury in glass thermometer graduated at intervals of 0.1^{o}. This reference thermometer was itself calibrated against a National Physical Laboratory certificated Platinum Resistance Thermometer which was reproducible to 1^{o} C $\pm 10^{-3}$ (Beg 1977).

2.2.3 Spectrophotometric Measurements - 1cm, quartz cuvettes were used for all spectrophotometric determinations. The buffer system used to control the pH of the solution under test was placed in the reference cell in all cases.

2.3 Glassware - Grade A volumetric flasks and Grade B pipettes were used throughout the study. Where necessary glassware was cleansed by immersion in chromic acid followed by a standard washing routine consisting of six rinsings with tap and six with distilled water. Sintered glass filters were cleaned by immersion in boiling concentrated potassium permanganate solution, followed by neutralisation with a dilute solution of hydroxylammonium chloride and repeated washing with tap and distilled water as before.

2.4 GENERAL METHODS - Chemical reagents were all of at least laboratory grade, buffer salts were AnalaR grade. Water was freshly distilled from an all glass still.

2.5 Model Solutes - These were obtained as reagent grade and recrystallised before use. Table 2.1 lists the supplier, recrystallisation solvent and melting points for the four model solutes used in this study.

Table 2.1 - Purification of the Model Compounds.

Compound	Supplier	Recrystallisation Solvent	Melting Point	
			Experimental	Literature *
Ethyl 4-aminobenzoate	BDH Ltd	50% ethanol	88°	88-89°
4-methoxy-benzoic acid	Sigma Ltd	absolute ethanol	183°	184°
phenol	BDH Ltd	40-60 petroleum ether	41°	40.85°**
4-nitro-phenol	BDH Ltd	toluene	113°	113-114°

* Merck Index (1976).
** Ultrapure material.

The four compounds were dried to constant weight prior to use in a vacuum oven.

2.6 PREPARATION AND CHARACTERISATION OF THE NYLON 6 POWDER

2.6.1 Preparation of Nylon 6 Powder

Nylon 6 was obtained from BDH Ltd in the form of injection moulding granules which were converted to powder form for use in sorption studies using the precipitation method described by Richardson (1973).

100 grammes of injection moulding granules were dissolved in 400ml of preheated 98% w/w formic acid at 60°. When dissolution was complete and the solution sufficiently mobile, the stirring rate was increased and 50% v/v aqueous methanol solution was added at a controlled rate to effect precipitation. The precipitate was filtered on a glass sinter, repeatedly washed with distilled water, then partially dried at 60° in a circulating air oven. The powder was passed through a number 10 sieve to remove large particles then dried again at 60° to constant weight in a vacuum oven. When dry, the powder was sieved again and three sieve size fractions collected, particles retained by a 60 mesh sieve, particles not retained by the 60 mesh sieve but retained by a 120 mesh sieve and all particles sub 120 mesh sieve size. The powder was stored in a desiccator over silica gel until used. Sieve mesh sizes refer to standard sieves (British Standard 410 (1962)).

2.6.2 Nylon 6 Powder Characterisation

2.6.2.1 Melting Point

The melting point was 214° measured with reference to dicyandiamid, a test substance melting at 210°. This compares to the literature value of 215° (Brydson, 1970).

2.6.2.2 Alcohol and Water Extractive

2 gramme samples of nylon 6 powder were shaken with 20ml of 95% v/v ethanol or water at 50° for twenty-four hours. The ultraviolet spectrum of the filtered supernatant showed a constant low absorbance of 0.01 absorbance units within the range 220-350 nm. In all cases solutions of the model solutes were diluted at least twenty-five times prior to spectrophotometric assay, therefore, the interference,

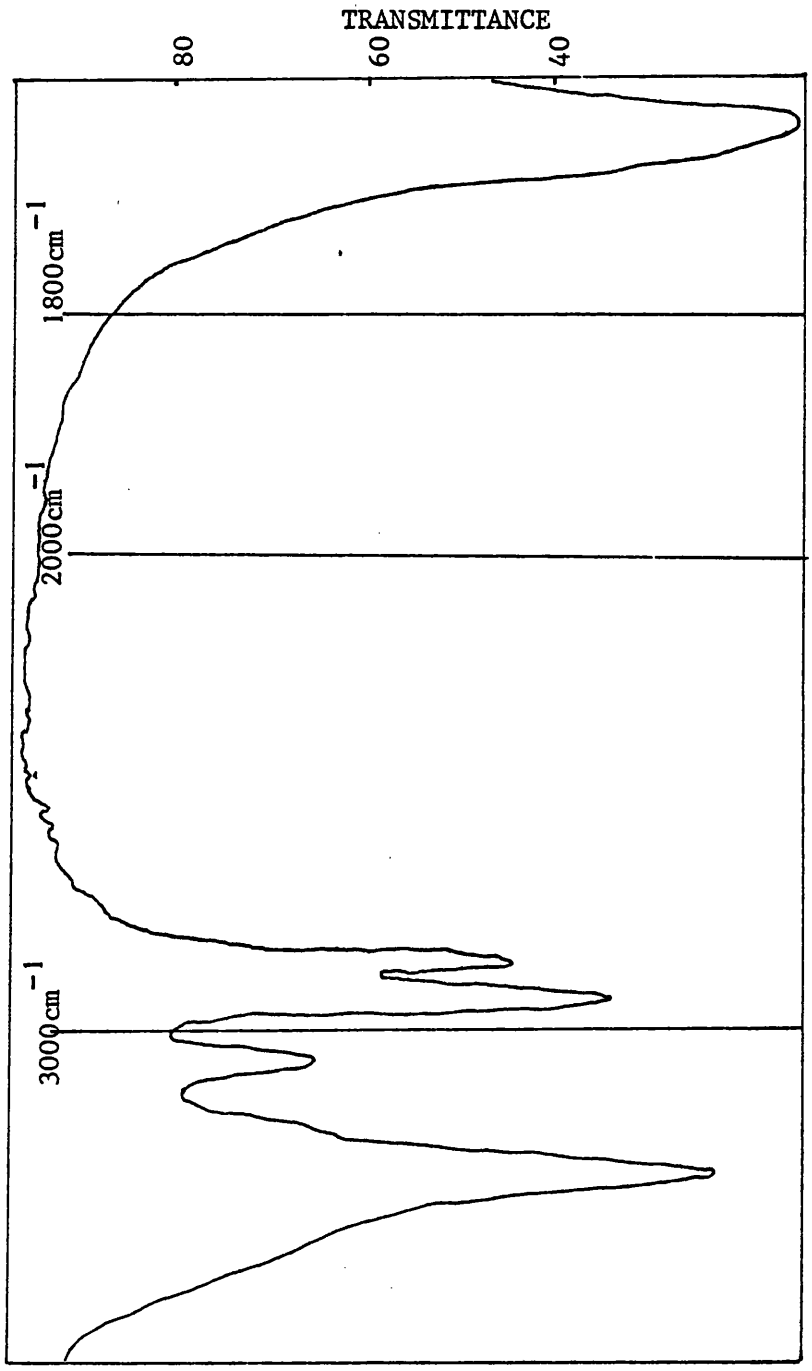


Figure 2.1 INFRA RED SPECTRUM OF NYLON 6 POWDER.

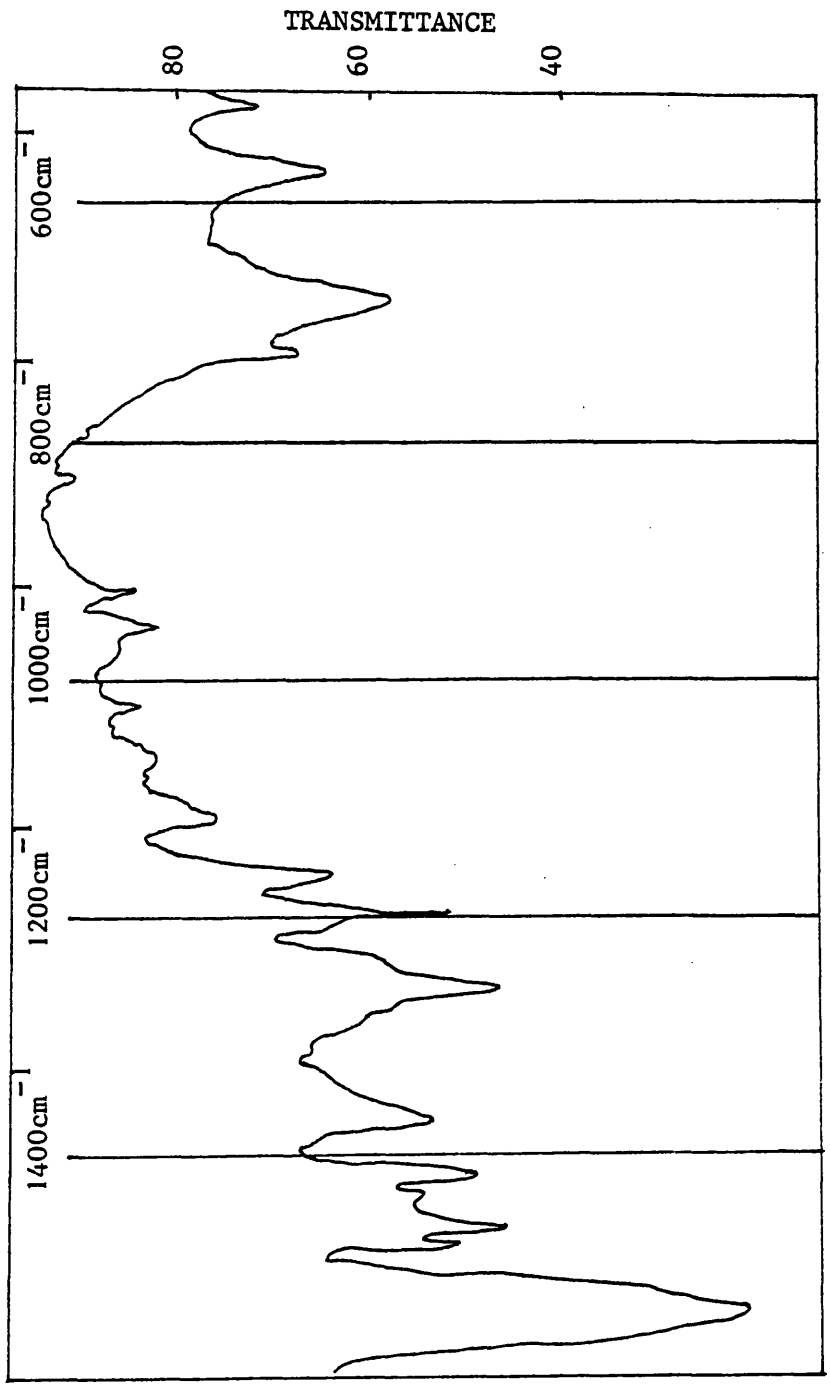


Figure 2.1 INFRA RED SPECTRUM OF NYLON 6 POWDER

Continued /.....

due to leached substances, was considered negligible.

2.6.2.3 The Infra-red Absorption Spectrum of Nylon 6 Powder

Figure 2.1 shows the Infra-red absorption spectrum of nylon 6 powder, determined by the Physicochemical Measurements Unit, Harwell. The powder was cold pressed into a thin film prior to analysis. The spectrum shows characteristic strong absorption bands at 3270, 2899, 1639, 1550 and 1460 cm^{-1}, corresponding to the amide groups in the nylon 6 matrix. The absence of a strong absorption band at 870 cm^{-1} indicates that free unpolymerised monomer is not present in significant quantity.

2.6.2.4. The Determination of Average Molecular Weight by Dilute Solution Viscometry.

The viscosity average molecular weight of the nylon 6 sample can be determined by relative viscosity measurements of moderately dilute solutions of the polymer using a capillary tube viscometer. The Mark-Houwink equation, equation 2.1, relates the viscosity average molecular weight M_v to the intrinsic viscosity η using two constants, K_m and α, which are valid for a particular polymer-solvent combination under specified physical conditions.

$$\eta = K_m \cdot M_v^{-\alpha} \quad \ldots\ldots\ldots\ldots \quad (2.1)$$

The intrinsic viscosity may be determined by measurement of the relative viscosity of a series of polymer solutions of different concentration, the relative viscosity (ηrel) being defined as the ratio of the polymer solution viscosity to solvent viscosity. The concentration dependence of ηrel is given by equation 2.2 the modified Einstein equation.

$$\eta rel = 1.0 + ac + bc^2 \quad \ldots\ldots\ldots\ldots (2.2).$$

Where a and b are constants and c is the polymer solution concentration in gramme dl^{-1}. A plot of the reduced specific viscosity, $(\eta rel - 1)/c$, against concentration is linear, the intrinsic viscosity is then obtained by extrapolating the slope to zero concentration where the reduced specific viscosity equals the intrinsic viscosity. K_m and α have been determined for nylon 6 in 85% w/w aqueous formic acid solution at 25° (Polymer Handbook 1967) which are valid between molecular weights of 5,000 - 50,000

$K_m = (2.26 \pm 0.2) \times 10^{-4}$ $\alpha = 0.82 \pm 0.03$

Method

A specially modified BS/IP/SL.2 suspended level viscometer was used with an enlarged reservoir to permit dilution to be performed in the viscometer. All pipettes used were calibrated to ensure that the exact delivery volumes were known. 15ml of 85% w/w formic acid was placed in the viscometer and equilibrated to temperature, the flow time was then determined. 10ml of a nominal 6.0 g dl^{-1} stock solution of nylon 6 in 85% w/w formic acid was then added and the flow time redetermined after thorough mixing of solvent and solution. This procedure was repeated with successive 5 ml quantities of 85% w/w formic acid. As all flow times were in excess of 350 seconds kinetic energy corrections were ignored. Flow time determinations were repeated until three successive flow times agreed to within 0.2%, timed accurately to 0.1 seconds. The density of the most concentrated nylon 6 solution differed from that of the solvent by 0.04%, density corrections were therefore ignored.The relative viscosity was thus calculated from the ratio of the solution to solvent flow

times. Data for two separate intrinsic viscosity determinations are shown in Table 2.2 and plotted in Figure 2.2

Table 2.2 Data for the determination of the intrinsic viscosity of Nylon 6 in 85% w/w formic acid at 25°.

Concentration ($g\ dl^{-1}$)	Determination I		Determination II	
	mean flow time (secs)	reduced specific viscosity ($dl\ g^{-1}$)	mean flow time (secs)	reduced specific viscosity ($dl\ g^{-1}$)
0.0	389.6	-	402.4	-
0.611	641.8	1.059	662.4	1.057
0.509	599.2	1.047	617.0	1.048
0.437	565.9	1.036	584.0	1.035
0.382	542.3	1.026	560.3	1.027
0.340	524.6	1.019	541.5	1.017
0.306	510.2	1.012	527.5	1.015

The data in Table 2.2 was submitted to a least-squared regression analysis to determine the intrinsic viscosity, and the two intercepts for each determination compared by t-test. Table 2.3 summarises the results. The two intercepts were not significantly different, at the 95% level of significance, therefore, a mean value of 0.968 $dl\ g^{-1}$ gave a viscosity average molecular weight of 26,900.

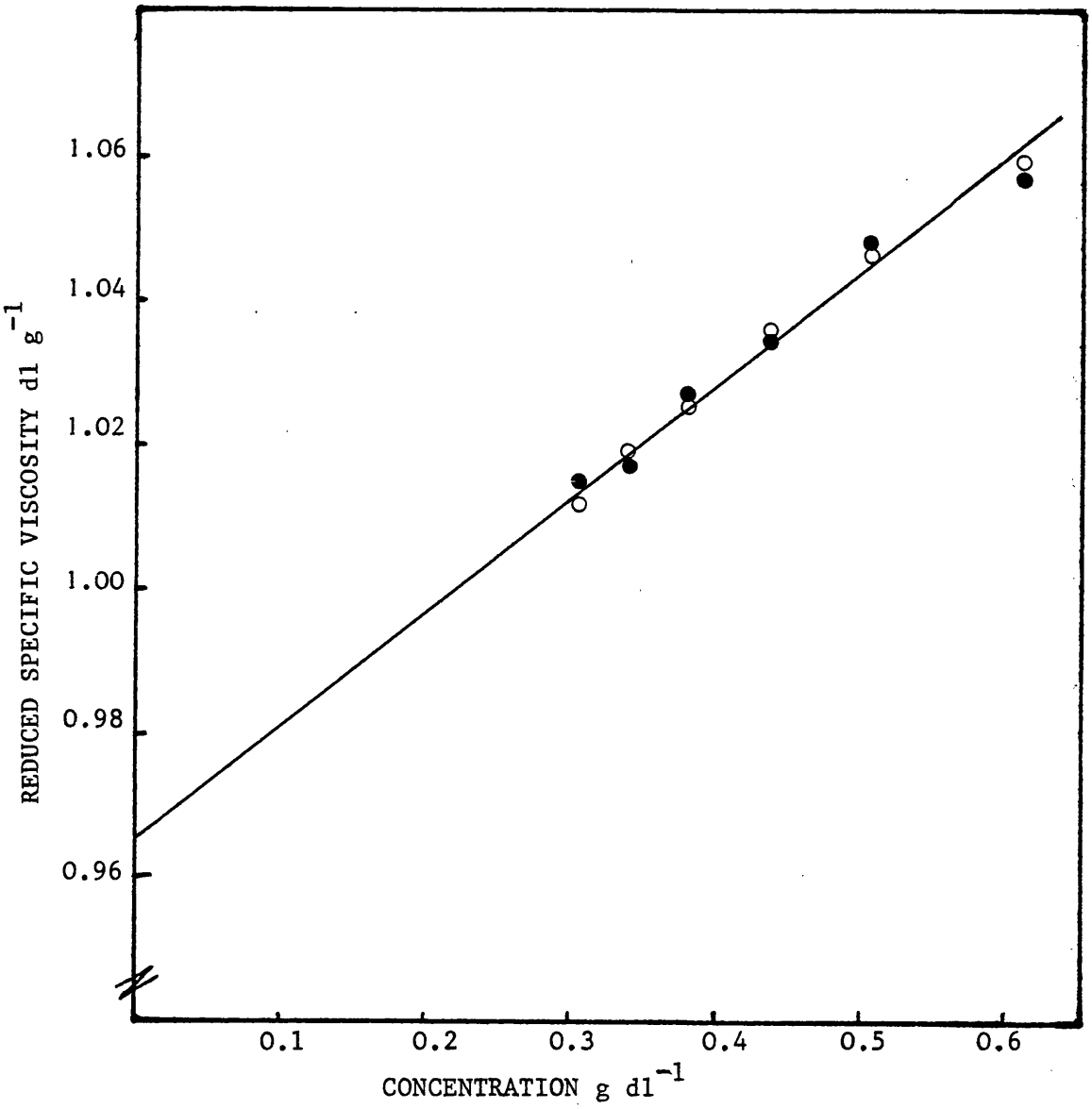


FIG 2.2 PLOT OF REDUCED SPECIFIC VISCOSITY VERSUS NYLON 6 CONCENTRATION IN 85% FORMIC ACID AT 25°

Table 2.3 Data from the least-squares regression analysis of the intrinsic viscosity determination of nylon 6 in 85% w/w formic acid at 25°

Intrinsic Viscosity $dl\ g^{-1}$	Standard Error of Intrinsic Viscosity $dl\ g^{-1}$	t_{calc}	t_{tab} (P=0.05)
0.966	3.3×10^{-3}	0.71	2.31
0.970	4.6×10^{-3}		

2.6.2.5 Surface Area Determination using Krypton Gas Adsorption.

The specific surface area of an adsorbent material can be determined by adsorbing inert gases on to the surface at low temperature. V_m, the volume of gas adsorbed to form a monolayer can be determined from the adsorption isotherm using the linear form of the B.E.T. equation (Brunauer et al 1938). Equation 2.3

$$P/V(P_o-P) = 1.0/V_m b + (b-1)\ P/V_m\ b\ P_o \quad \text{.....(2.3)}$$

where: P = gas pressure at which a volume, V, of gas is adsorbed

P_o = the saturated vapour pressure at S.T.P

V_m = the monolayer volume capacity of the adsorbate

b = a constant

A straight line results if $P/V(P_o-P)$ is plotted against P/P_o and the value V_m can be calculated from the slope $(b-1)/V_m b$ and the intercept

$1/V_m b$. The equation is valid between reduced pressure, P/P_o between 0.05 - 0.3 and will give reliable values of V_m when the constant b has a high value due to a well defined plateau in the isotherm corresponding to monolayer formation. When solids have a high specific surface areas, errors involved in the experimental determination of V_m greatly exceed the uncertainty of the B.E.T. method. This is not the case, however, with low specific surface area adsorbates when only a small fraction of gas is adsorbed. In such cases the amount of gas adsorbed cannot be accurately determined in a constant volume apparatus as the pressure difference between the gas before and after adsorption is too small to be reliably measured. Richardson (1973) reported a specific surface area for nylon 6 powder of the order 6 m^2g^{-1}. The use of Krypton at -196^o with P_o approximately equal to 2 mm Hg keeps working pressures low enough to keep the correction for unadsorbed gas small. (Young and Crowell, 1962).

Method.

The apparatus used for determining the B.E.T. surface area of nylon 6 powder is shown in figure 2.3. A known weight of powder was placed in the sample bulb and degassed under high vacuum at room temperature for twenty-four hours. At the commencement of the determination the sample bulb was immersed in boiling liquid nitrogen to maintain the sample at -196^o, the rest of the apparatus was at ambient temperature which was noted for the calculation of V_m. Krypton gas was admitted into the apparatus through the gas lock between valves D and E and allowed to expand into the volume enclosed between the McCleod gauge and values A and B. The initial volume of gas could

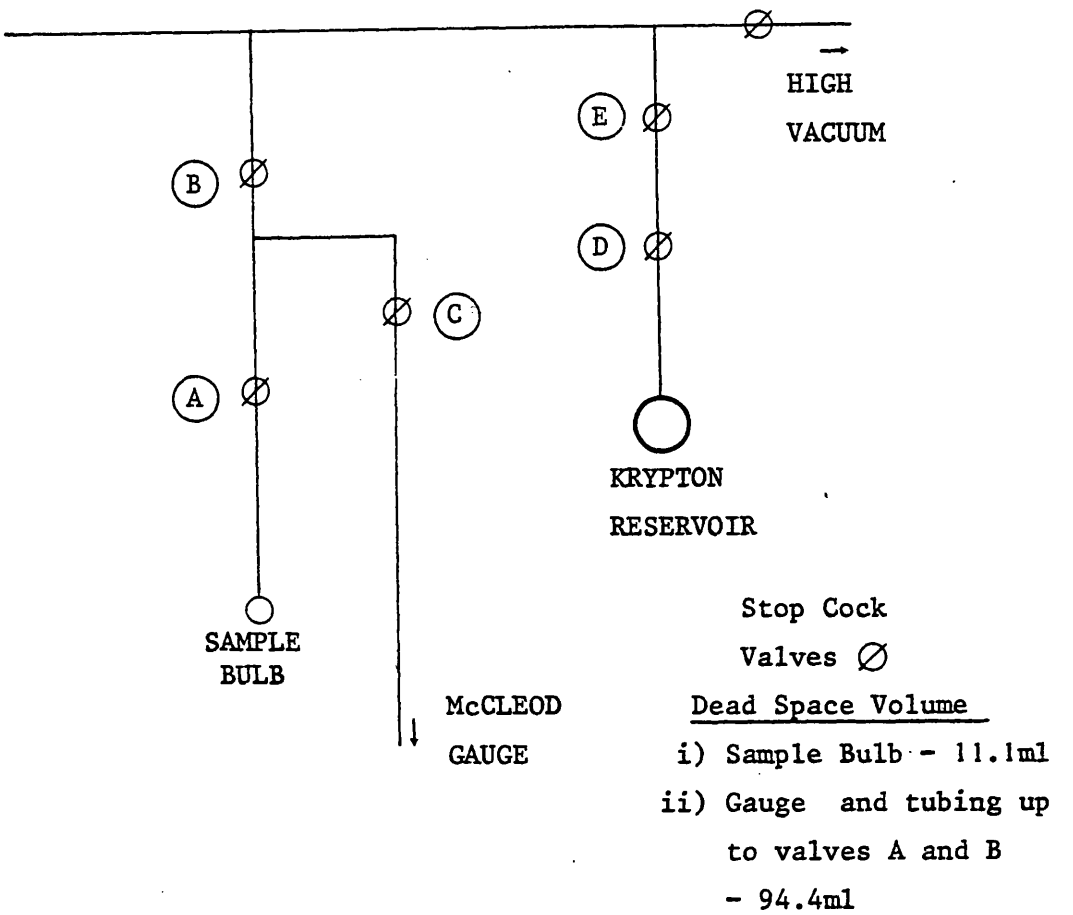


Figure 2.3 Schematic Diagram of the B.E.T. apparatus used for the Surface Area Determination of Nylon 6 Powder.

now be measured, using the gauge, by determining the pressure of the gas in the known volume of the gauge system. Gas was then expanded through valve A into the sample bulb and allowed to equilibrate; at equilibrium the volume of gas unadsorbed was redetermined. This procedure was repeated for several values of reduced pressure to generate data for the B.E.T. isotherm. Data for replicate determinations of the B.E.T. surface area of the nylon 6 powder fraction retained by the 120 mesh sieve is shown in table 2.4 and plotted in figure 2.4.

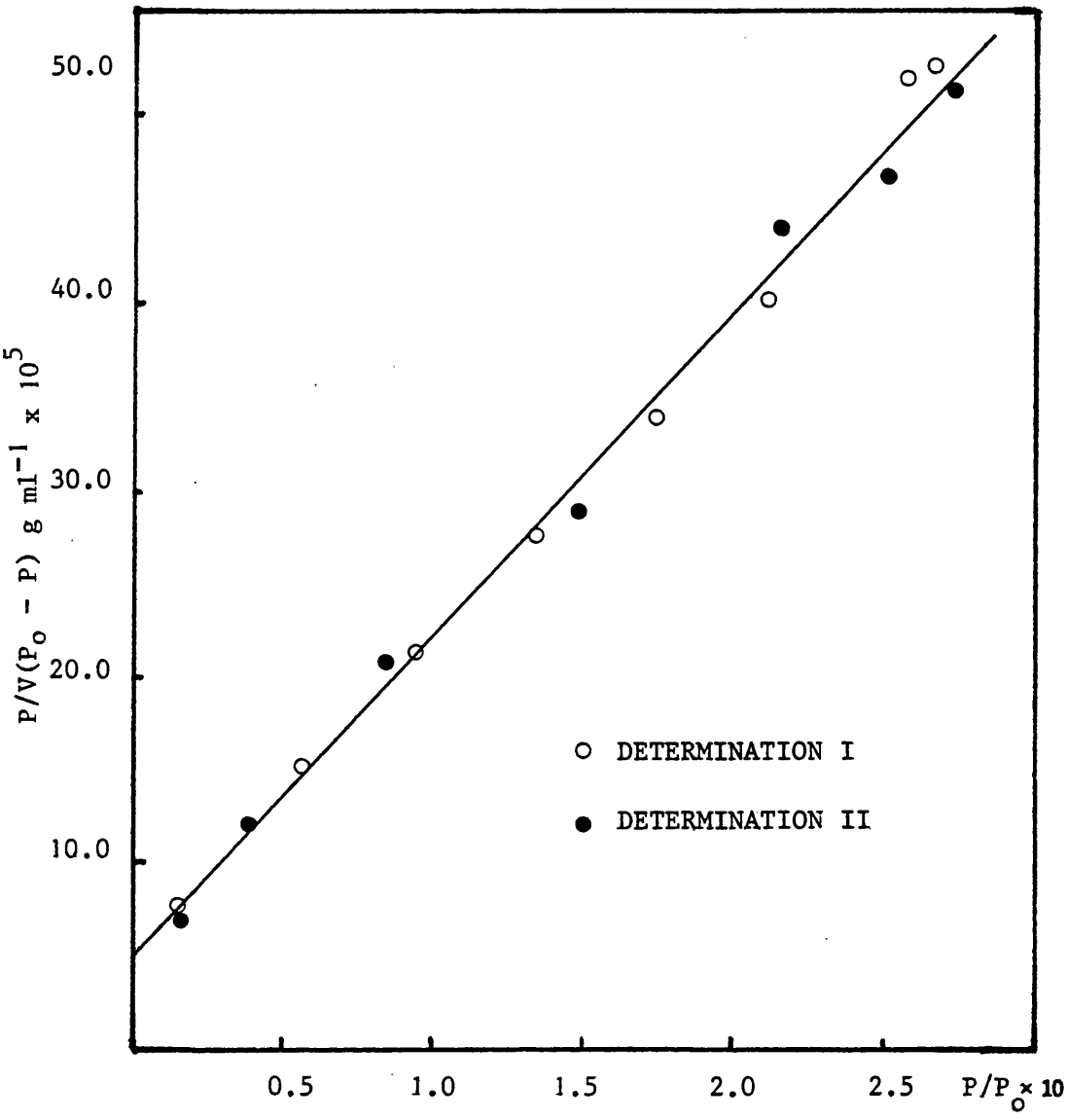


FIG 2.4 B.E.T PLOT OF THE SURFACE AREA DETERMINATION OF NYLON 6 POWDER (60 - 120 mesh) BY KRYPTON ADSORPTION AT -196°

TABLE 2.4 Data for the Determination of the B.E.T. Surface Area of Nylon 6 Powder (sub 60, retained by 120 mesh size) using Krypton Adsorption at -196°

Krypton Pressure initial mm Hg	Krypton Pressure equilibrium mm Hg	Volume adsorbed ml g^{-1}	P/P_o	$\frac{P}{V(P_o-P)}$ g $ml^{-1} \times 10^5$
Determination 1 - Ambient temperature 19.0°				
0.366	0.031	4.55	0.016	7.74
0.407	0.108	8.53	0.055	15.02
0.356	0.186	10.74	0.094	21.40
0.382	0.263	12.25	0.134	27.76
0.443	0.340	13.55	0.173	34.01
0.469	0.418	14.14	0.212	42.01
0.562	0.505	14.80	0.256	51.48
0.531	0.521	14.96	0.264	53.15
Determination 2 - Ambient temperature 19.0°				
0.294	0.026	3.26	0.013	7.21
0.268	0.072	5.60	0.087	12.01
0.407	0.165	8.44	0.084	21.40
0.505	0.294	10.85	0.149	28.60
0.531	0.423	11.99	0.215	40.43
0.567	0.495	12.80	0.251	46.28
0.583	0.536	13.33	0.272	49.61

The data in table 2.4 was submitted to least-squared regression analysis for accurate assessment of the slope and intercept, to calculate V_m, the results are shown in table 2.5

Table 2.5 Results for the Least-Squares Regression Analysis of B.E.T. Plots for the Adsorption of Krypton by 60-120 Mesh Nylon 6 Powder.

Determination	Slope $g\ ml^{-1}$	Standard Error	Intercept $g\ ml^{-1}$	Standard Error	V_m $ml\ g^{-1}$
I	1.83×10^{-3}	5.60×10^{-5}	3.91×10^{-5}	1.04×10^{-5}	534.7
II	1.64×10^{-3}	3.57×10^{-5}	4.96×10^{-5}	7.35×10^{-6}	591.8

The B.E.T. surface area can be calculated using V_m and equation 2.4, V_m is corrected to its corresponding value at S.T.P which allows the volume of gas in the monolayer to be converted to the number of mols of gas. Using Avogadro's number and the surface area per Krypton molecule, taken as $20 \times 10^{-20}\ m^2$ at -196^o, the surface area of the adsorbent may be calculated assuming that the total surface area of the molecules comprising the monolayer is equivalent to the actual surface area.

$$S_w = \frac{V_m . N . x}{\bar{V}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.4)$$

where: S_w = the specific surface area.

N = Avogadro's number.

x = the area of one gas molecule at -196^o

$\bar{V}$ = molar volume of gas at S.T.P.

Surface areas for the three nylon 6 powder sieve size fractions are given in table 2.6

Table 2.6 Specific Surface Areas for Nylon 6 Powder Samples Determined by Krypton Gas Adsorption

Sieve Mesh Size	Determination	Specific Surface Area $m^2 g^{-1}$
retained by 60	I	5.12
	II	5.15
60 - 120	I	3.53
	II	3.90
sub 120	I	4.34
	II	4.13

2.6.2.6 Determination of the Pore Volume and Pore Size Distribution of Nylon 6 Powder using a Mercury Porosimeter.

The mercury porosimeter determines the total pore volume and pore size distribution of a solid material by incrementally forcing a given amount of mercury into the solid sample at high pressure and simultaneously measuring the volume of mercury taken up. The sample is placed in a glass dilatometer consisting of a bulb and stem which enclose a capillary of known dimension. After degassing, the dilatometer is filled with mercury under vacuum until the bulb and capillary are almost full. The filling apparatus is returned to atmospheric pressure, and the dilatometer removed and fitted into the porosimeter autoclave which is filled with ethanol which acts as hydraulic fluid transmitting the pressure applied by the compressor to the mercury. The applied pressure can be related to the pore radius using the modified Young-Laplace equation, equation 2.5

$$P = \frac{2\gamma \cos\phi}{r} \qquad \text{.....(2.5)}$$

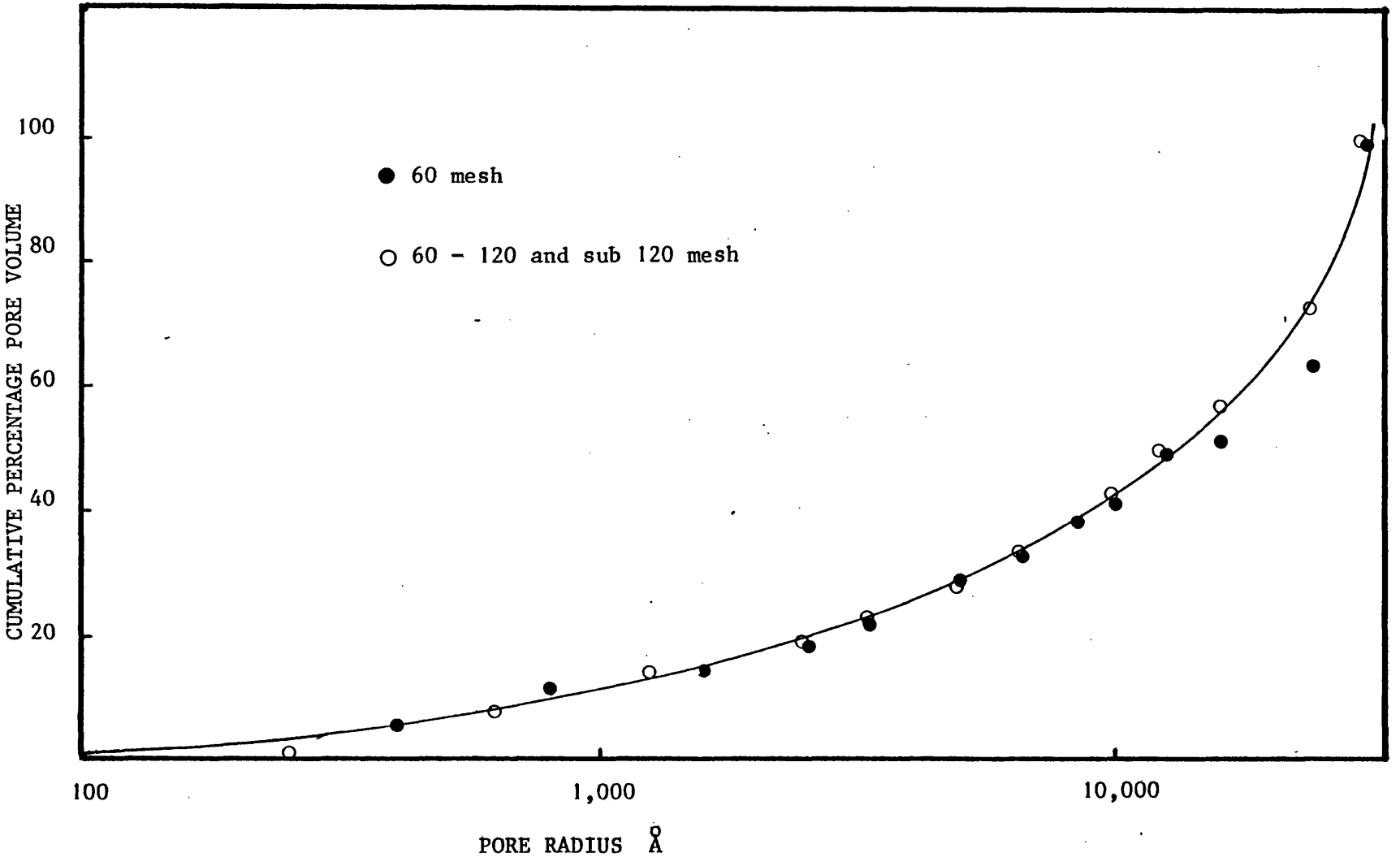
where P = applied pressure γ = mercury solid interfacial tension

ϕ = mercury solid contact angle r = pore radius (pores assumed cylindrical)

The instrument applies a pressure which will force mercury into all pores greater than and including those of the radius defined by equation 2.6. The increased extent of intrusion will cause a drop in the mercury level in the dilatometer capillary which is converted to volume knowing the cross sectional area of the capillary and the displacement. The instrument applies the pressure, in increments, automatically, and pauses after compression to allow a mercury contact probe to assess the extent of mercury uptake. The size distribution can be represented by a plot of cumulative percentage pore volume vs pore radius, the porogram, and the total pore volume may be obtained from the total volume of mercury taken up by the solid. The operating range of the instrument is defined by the pressure it is able to exert, in this case the range is 50 - 75,000 Å.

Porograms for the three nylon 6 powder size fractions are shown in figure 2.5, where it can be seen that there is no apparent difference in pore size distribution between the samples. Although the operational pore radius range of the instrument is 50 - 75,000 Å, the actual particle pore size distribution was taken to commence at 30,000 Å. The percentage cumulative pore volume reduced rapidly from 75,000 to 30,000 Å which has been suggested to result from compression of the powder mass resulting in the determination of packed-bed rather than true intraparticle pore volume (England, Personal Communication). The total pore

FIG 2.5 CUMULATIVE PERCENT PORE VOLUME VS RADIUS FOR NYLON 6 POWDER



volume for 60 mesh nylon 6 powder is $7.1 \times 10^{-2} cm^3 g^{-1}$ and for 60 - 120 and sub 120 mesh sizes, 4.1×10^{-2} cm^3 g^{-1}, although the total pore volume is different, the cumulative pore size distributions for the three size fractions is similar. Dubinin (1960) has classified pores into three size ranges; micropores intermediate pores and macropores with size ranges less than 10Å, 10 - 1000Å and greater than 1000Å respectively. As the porogram is with respect to the pore radius axis it can be assumed that the linear limit of the pore volume distribution has been reached, Nylon 6 powder is not microporous and has 11% of its pore volume in the upper transitional pore region and 89% in the macropore region.

2.6.2.7 Determination of the True Density of Nylon 6 Powder

The true density of nylon 6 powder was determined using a helim-air pycnometer. The instrument consists of an airtight sample chamber connected to a low pressure helium supply, a vacuum and a pressure gauge. The pycnometer operates on the principle that the change in pressure of a nonadsorbing gas within an enclosed vessel due to the presence of a volume of powder sample, is a function of the volume of the solid material within the vessel. The sample density was measured by determining the pressure of gas in the empty chamber, then redetermining the pressure with a known weight of sample of unknown density. This procedure is then repeated with a standard volume stainless steel ball. The volume of the unknown sample volume is determined using equation (2.6)

$$V_{sample} = \frac{V_{standard} \ (R_E - R_{SA})}{(R_E - R_{ST})} \quad \ldots\ldots\ldots\ldots (2.6)$$

Where, V is volume and R is the pressure gauge vernier reading. R_E is the pressure determination reading for the empty chamber, R_{SA}, that for the sample and, R_{ST}, the pressure reading for the standard volume. The density is then obtained by dividing the sample weight by the volume as determined by the pycnometer. The temperature was monitored throughout the determination which must remain constant for the duration of the measurement. Replicate determinations using the helim-air pycnometer give true density values of 1.18, 1.17 and 1.17 g cm^{-3} for 60 mesh, 60 - 120 mesh and sub 120 mesh nylon 6 powder size fraction respectively compared to the literature value of 1.04 - 1.14g cm^{-3} (Roff 1971).

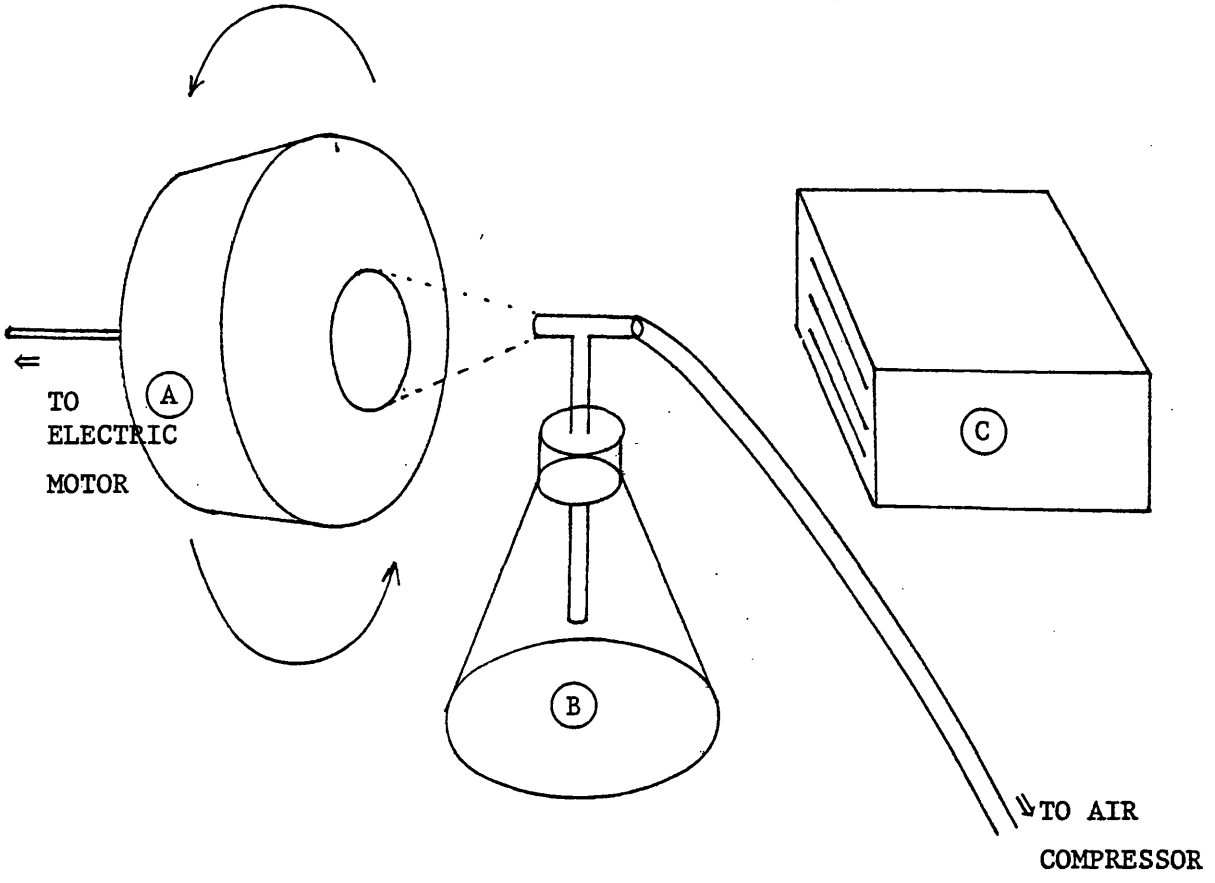
2.6.2.8 Scanning Electron Microscopy of the Nylon 6 Powder

The polymer was initially covered in gold under vacuum to prevent surface charging in the electron beam, theexcitation potential used was 16 KV to reduce structural damage due to the impinging electron beam. The surface features recorded photographically are stable with respect to time and have been interpreted as a real representation of the surface; electron micrographs of the nylon 6 powder surface are shown in section

2.7 PREPARATION and CHARACTERISATION of NYLON 6 COATED and UNCOATED ACTIVE CARBON for use in ADSORPTION STUDIES.

2.7.1 Description and Suppliers Technical Information for the Active Carbon Granules.

The active carbon granules used throughout this study were Sutcliffe Speakman 610 grade coconutshell active carbon granules, 5 - 10 mesh size, which had been subjected to a special cleaning procedure by Smith and Nephew Ltd, and were obtained, as a gift, from them. The cleaning procedure (Simmonite, 1977) consists of



A) Rotating Copper Pan Containing the Active Carbon Granules.

B) All Glass Spray-Gun Containing the Solution of Nylon 6, Coupled to an Air Compressor.

C) Domestic Hot Air Fan Directed Towards the Copper Pan.

FIG 2.6 : SCHEMATIC DIAGRAM OF THE APPARATUS USED TO APPLY A FILM OF NYLON 6 TO THE SURFACE OF THE ACTIVE CARBON GRANULES.

placing the granules in a column, supported by a mesh and washing with 50% v/v aqueous ethanol at a high flow rate, this will remove alcohol soluble contaminants together with heavy and light particulate impurities. The solid impurities are then skimmed off and the bed washed with hot water (60–70^{o}) to remove both the aqueous ethanol and any fine particles present. The carbon particle slurry is removed and dried. The technical specifications for the original granular material prior to washing as supplied by the original manufacturer were as follows:

B.E.T. Surface Area	using nitrogen gas - 1300–1500 m^2g^{-1}
	using benzene vapor - 1250–1350 m^2g^{-1}
Carbon tetrachloride saturation vapor uptake	85 - 95% w/w
Ash	3 - 4% w/w
Bulk density	0.4 - 0.44 g cm^{-3}

2.7.2. The Preparation and Characterisation of Nylon 6 Coated Active Carbon Granules.

The coating method was a small scale spray coating procedure based on the process used by Smith and Nephew (Research) Ltd, described by Simmonite (1977). The coating apparatus is shown in schematic form in figure 2.6. 100 grammes of carbon granules were rotated in the copper pan at 40 rpm in a stream of hot air such that the granule bed maintained a bulk temperature of 72^{o}. A 5% w/v solution of nylon 6 in formic acid was sprayed onto the warm granules from the all glass spray system, the spray atomised using a compressor. The formic acid evaporates off rapidly leaving a smooth polymer layer over surface of the granules. The spray cone was directed into the coating pan at a spray rate which minimised turbulence in the granule bed; the coat was applied in pulses to

allow sufficient time for the formic acid to evaporate before the next application. The coated active carbon used throughout this study was prepared from two, 100ml aliquots of spray solution per 100 grammes of charcoal granules. After coating, the granules were thoroughly washed with 50% v/v aqueous ethanol followed by five washings with distilled water. The granules were dried at 60°C to constant weight under atmospheric pressure before use.

2.7.3. Characterisation of the Uncoated and Nylon 6 Coated Active Carbon Adsorbents.

2.7.3.1 Alcohol and Water Extraction.

2 grammes of adsorbent granules were shaken with 50ml of water 95% v/v ethanol at 50° for twenty-four hours. The ultraviolet spectrum of the filtered supernatant showed constant low absorbances of 0.012 and 0.011 adbsorbance units for the uncoated and nylon 6 coated granules respectively, within the range 220-350 nm. In all cases solutions of the model adsorbates were diluted prior to spectrophotometric assay by a factor of at least twenty-five times, therefore the interference due to leached substances was considered negligible.

2.7.3.2. Determination of the Heat of Wetting by Organic Solvents.

Heats of wetting data may be used to determine whether the adsorbent granules will act as a molecular sieve when taking up pure organic liquids of different molecular weights. The heat of wetting for silicone oil (2 cp grade) and benzene were determined by the Chemical Defence Establishment, Porton Down using a recording microcalorimeter. The heats of wetting for silicone oil were 107 Jg^{-1} and 118 Jg^{-1} for the coated and uncoated material respectively.

Similarly for benzene, heats of wetting were 130 Jg^{-1} and 135 Jg^{-1} for the coated and uncoated adsorbents respectively. These differences in the values for the benzene and silicone oil heats of wetting cannot be considered significant and indicates that the carbon granules do not show a high degree of specificity with respect to differing solute molecular weight (Smith, Personal Communication).

2.7.3.3. Saturation Vapour Uptake of Organic Liquids by the Nylon 6 Coated and Uncoated Adsorbent Granules.

The saturation vapour uptake is a method of assessing the volume of the adsorbent available for the adsorption of low molecular weight molecules. The test sample is weighed, then placed in a desiccator containing the adsorbate, and maintained at a constant 25° in an incubator. The adsorbent will continue to take up the vapour until it is saturated which is taken to be complete when the sample weight is constant. The saturation vapour uptake is expressed as a weight percentage and a saturation volume uptake which may be obtained from the weight percentage using the liquid density. Table 2.7 summarises the saturation vapour uptake data. These data indicate that the volume available to the three test vapours is the same showing that the adsorbent granules exhibit no molecular sieve behaviour for compounds of molecular weight of less than 153.8.

Table 2.7 Saturation Vapour Uptake Data for Three Test Solvents on to Nylon 6 Coated and Uncoated Active Carbon at 25°.

Solvent	Molecular Weight	Percentage Saturation w/w		Saturation volume cm^3g^{-1}	
		uncoated	coated	uncoated	coated
carbon tetrachloride	153.8	104	99	0.65	0.62
benzene	78.1	58	55	0.66	0.63
chlorobenzene	112.6	71	70	0.65	0.63

2.7.3.4 Determination of Pore Volume and Size Distribution by Mercury Porosimetry.

The investigation of the porous nature of active carbon was identical to that of nylon 6 powder (see Section 2.6.2.6). The porogram for active carbon is shown in figure 2.7. The cumulative percentage pore volume curve is convex with respect to the pore radius axis indicating that the distribution is incomplete and that the porous structure of the active carbon granule continues below 50Å, the lower limit of sensitivity of the instrument. The active carbon granules have a total pore volume (between 50 - 75,000Å) of 0.269 cm^3g^{-1}, four times that of nylon 6 powder, 51% of the pore volume present as transitional pores, 49% as macropores. Microporosity is implied from the slope of the cumulative pore volume distribution curve which is convex to the pore radius axis.

The porogram for nylon 6 coated active carbon is shown in figure 2.8. It is not clear to what degree the porosity of the

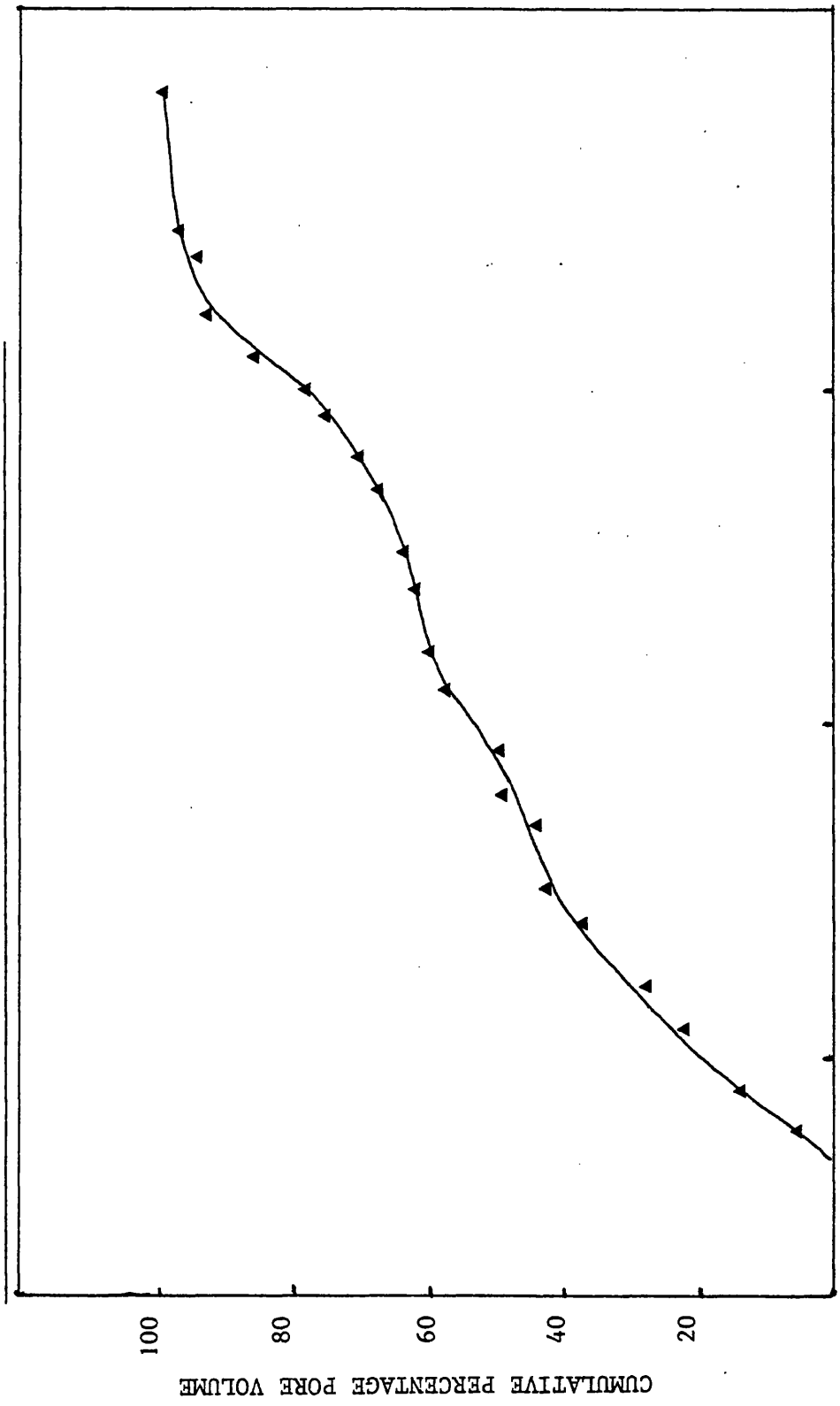


FIG 2.7 CUMULATIVE PERCENT PORE VOLUME VS RADIUS FOR ACTIVE CARBON

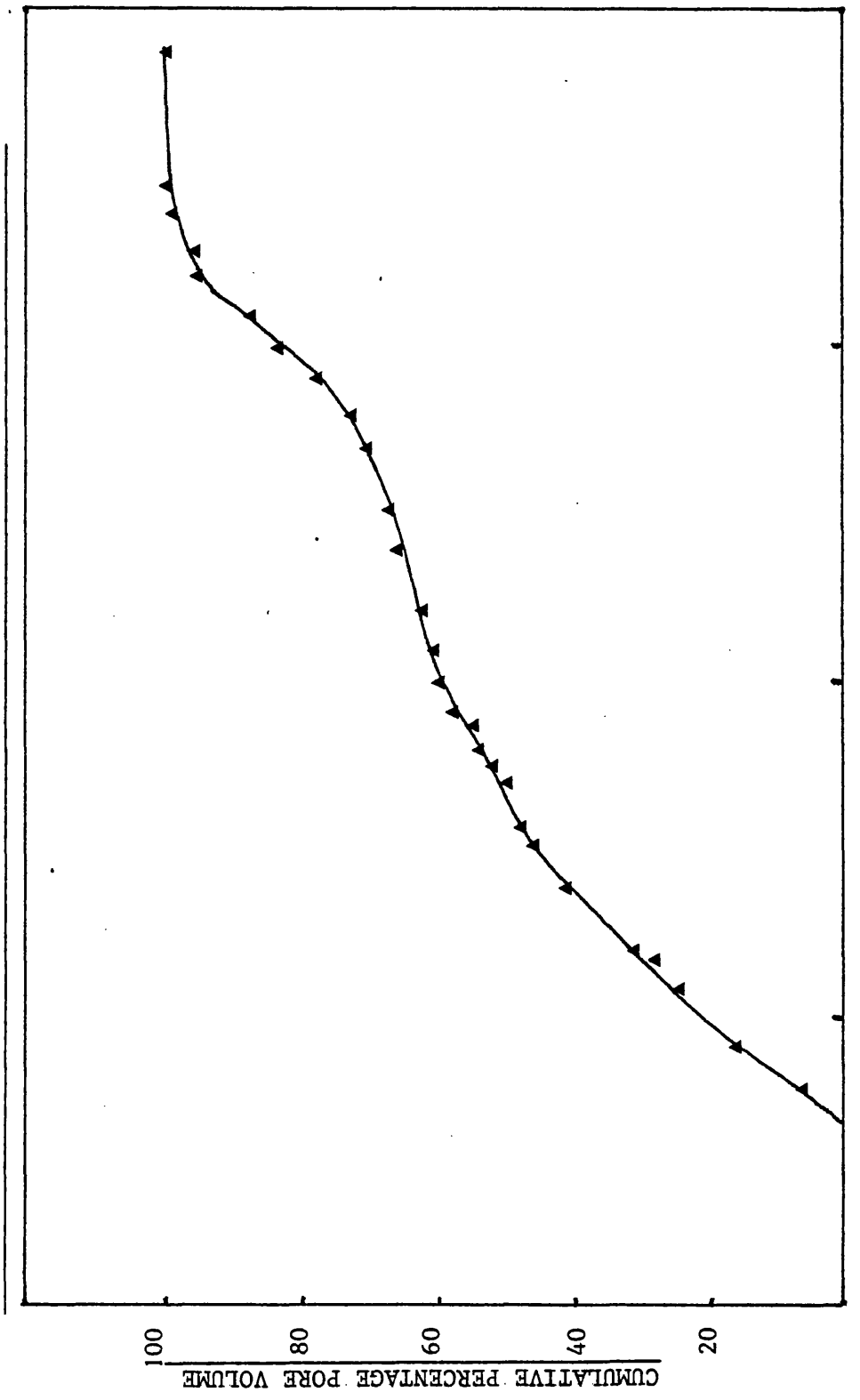


FIG 2.8 CUMULATIVE PERCENT PORE VOLUME VS RADIUS FOR NYLON 6 COATED ACTIVE CARBON

coated material is characterised by this technique. The extent of damage inflicted on the coat by the application of the high vacuum during the dilatometer filling process must be taken into consideration when interpreting the porogram for the coated material.

SORPTION STUDIES

3.1 ASSAY PROCEDURES

Assays for solute concentration for both single solute and binary solute solutions were carried out using ultraviolet spectrophotometric methods.

3.1.1 Assay of the Concentration of Single Solute Solutions.

The absorbance, A, of a solute of molar concentration, C, at a given wavelength is given by the Beer-Lambert relationship (equation 3.1).

$$A = E_m \times c \times 1 \quad \ldots\ldots\ldots\ldots \quad (3.1).$$

E_m is the molar extinction coefficient and 1 is the solution path length. A plot of absorbance versus molar concentration at the wavelength of maximum absorbance, the λ_{max}, is typically linear over the range 0 - 0.7 absorbance,units, where the slope is equal to the molar extinction coefficient, E_m. The molar concentration of a solution of unknown concentration may then be determined using equation 3.1 by measuring the absorbance of the solution under test, at the λ_{max}, and by applying the E_m value to obtain the concentration. The spectrophotometric assays were carried out in McIlvaine's buffer at pH 2.32 or pH 8.0 at a controlled ionic strength. (Elving et al 1956). The buffer at pH 2.32 was formulated at 0.5M ionic strength and the pH 8.0 buffer at 1.0M. Selection of these pH values ensured that the solutes were either fully ionised or unionised. The E_m values were determined from replicate calibration experiments using solutions of known concentration. Data from the calibration plot was submitted to a computerised linear least-squares regression analysis

to obtain the molar extinction coefficient E_m and the intercept on the ordinate axis. In all cases the intercepts were within two standard deviations of the origin and the calibration curves all showed high linear correlation coefficients. The calibration plots all therefore obeyed the Beer Lambert Law over the range of the absorbance studied. The system is, therefore, fully described using the molar extinction coefficient and this value, together with its associated standard deviation will be presented in the tables. The E_m values obtained from two replicate determinations were compared using a t-test (Appendix 1). The two values for each solute were not significantly different at the 95% level of significance and the mean of the two values was, therefore, used in subsequent calculations. Values of λ_{max} and E_m for the four model solutes are given in table 3.1. The pK_a values quoted in table 3.1 for phenol and 4-nitrophenol are not corrected for ionic strength. The analytical pH of 2.32 is, however, significantly lower than 10.0 and 7.15 (the pk_a values of phenol and 4-nitrophenol) therefore small changes in pk_a due to ionic strength affects can be ignored.

3.1.2 Assay of Solute Concentrations in Binary Solute Solution.

Spectrophotometric methods may be employed to estimate the concentration of compounds in binary solute solution, provided that the absorption of the minor component can be either subtracted or neglected (Beckett and Stenlake 1970).

Table 3.1 Spectrophotometric Assay Data for the Four Model Solutes.

Solute	λ max nm	pK_a	percent unionised	analytical buffer pH	E_m	Standard Deviation	t^{***}_{calc}	Mean E_m
ethyl 4-aminobenzoate	285	2.57*	99.99	8.0	17132 17275	133 161	0.68	17204
4-methoxybenzoic acid	246	4.47*	0.01	8.0	13450 13206	150 78	1.44	13328
phenol	270	10.00**	99.99	2.32	1476 1474	20 42	0.04	1475
4-nitrophenol	319	7.15**	99.99	2.32	9857 9812	68 79	0.43	9835

* Richardson 1973 - Ionic strength 0.5M
** Albert and Sargeant - Ionic strength not specified
*** t_{tab} (P=0.05) - 2.31

Two cases of mixed absorption spectra typically arise in this type of analysis and these are illustrated schematically in figure 3.1

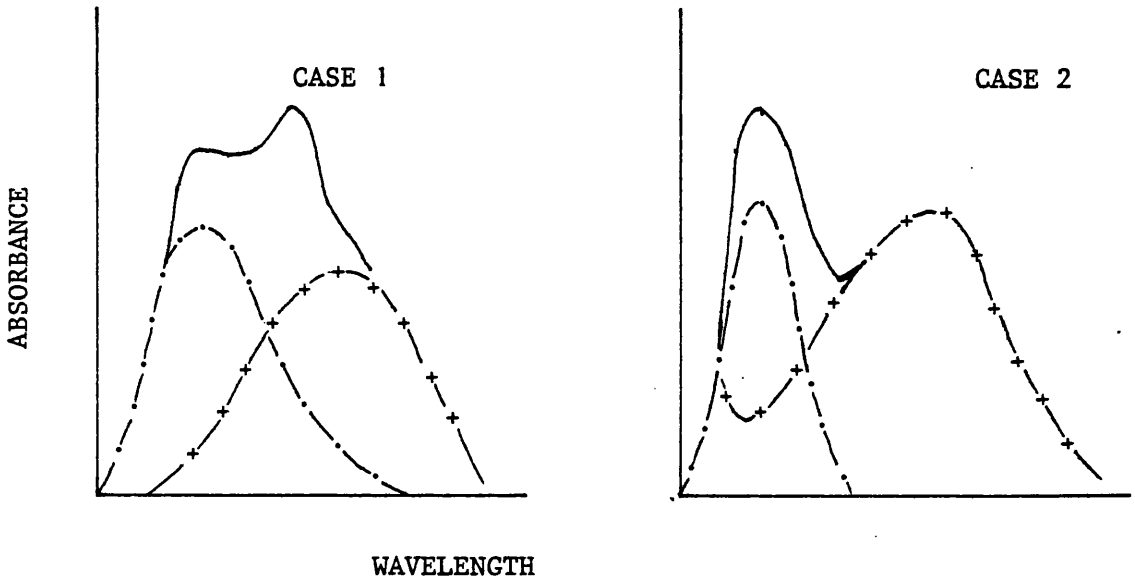


Figure 3.1 Schematic Representation of Mixed Absorption Spectra Typical of the Spectrophotometric Analysis of Binary Solute Solutions.

Case 1 shows that there is mutual interference by each component at the maximum absorbance of the other, hence the total absorbance depends upon two independently variable and unknown concentrations. Resolution of the mixture is however possible by measuring the composite absorbance at two wavelengths corresponding to the λ_{max} of each component and solving the Beer Lambert equation in the form of two simultaneous linear equations.

$$Abs_{\lambda_a} = (E^A_{\lambda a} \times C^A + E^B_{\lambda a} \times C^B) \times 1 \quad \ldots\ldots(3.2)$$

$$Abs_{\lambda_b} = (E^A_{\lambda b} \times C^A + E^B_{\lambda b} \times C^B) \times 1 \quad \ldots\ldots(3.3)$$

where

Abs = absorbance

E = molar extinction coefficient

C = molar concentration

1 = cell path length (1 cm)

λ_a = wavelength of maximum absorption of solute A

λ_b = wavelength of maximum absorption of solute B

Equations 3.2 and 3.3 can be solved to yield values of C^A and C^B provided that all other values are either known or can be experimentally measured. Assays for ethyl 4-aminobenzoate in the presence of 4-nitrophenol and 4-methoxybenzoic acid were both examples of case 1 type behaviour (figure 3.1). Absorption spectra and extinction coefficient data are given in figure 3.2 and 3.3 and tables 3.2 and 3.3 respectively. In most cases, the buffers used in the experimental determination and the analytical determination were at a constant ionic strength of 0.5 M. The isotherm determinations from aqueous ethyl 4-aminobenzoate were not carried out at constant ionic strength, the assay of this system was not therefore at 0.5 M ionic strength. The pH change associated with small changes in ionic strength arising from dilution prior to assay was considered neglibile as the pH of the analytical detemmination was in excess of 5 units above the pK_a of ethyl 4-aminobenzoate.

The assay of ethyl 4-aminobenzoate in the presence of 4-nitrophenol was carried out at pH 2.32 where a satisfactory resolution of

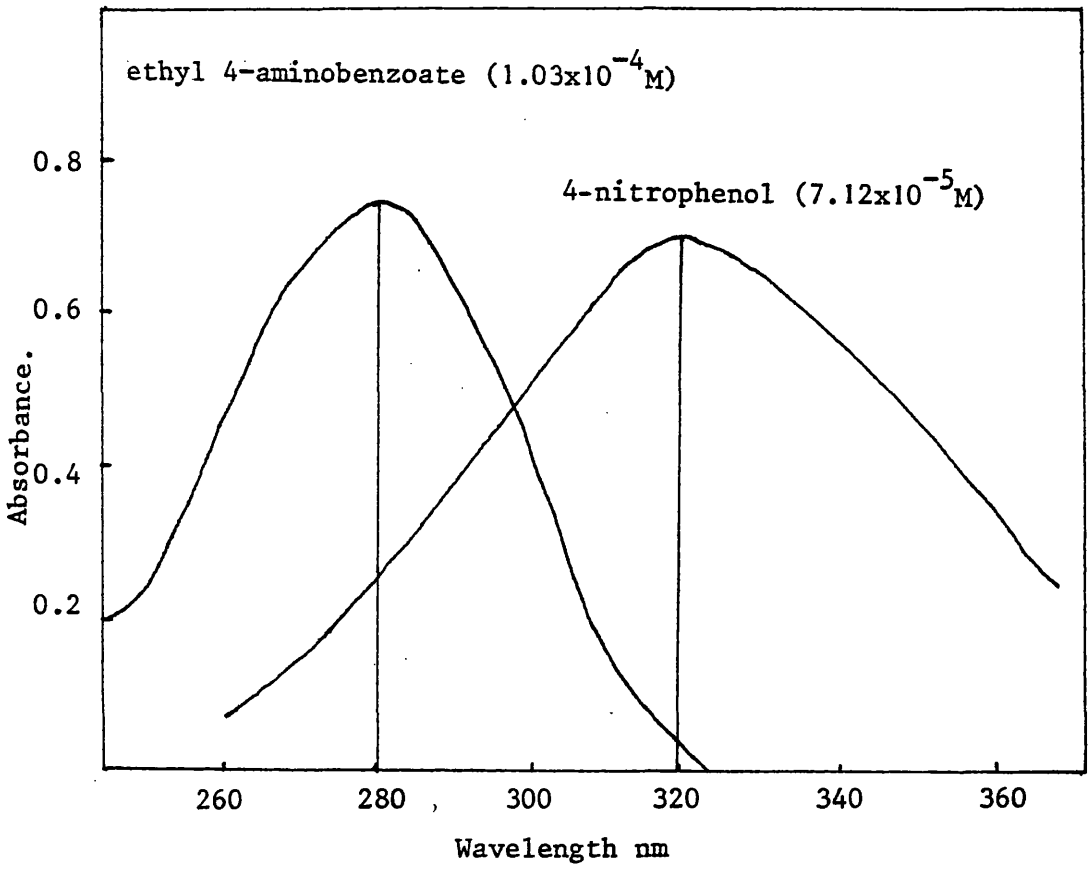


Fig 3.2 Absorption Spectra for Ethyl 4-aminobenzoate and 4-nitrophenol at pH 2.32 (0.5M Ionic Strength)

Table 3.2 Spectrophotometric Data for the Ethyl 4-aminobenzoate : 4-nitrophenol Mixed Assay at pH 2.32 (ionic strength 0.5M).

Solute	Wavelength	Molar Extinction Coefficient	Standard Deviation	t_{calc}*	Mean Molar Extinction Coefficient
4-nitrophenol	319	9857	68	0.43	9835
		9812	79		
	280	4039	14	0.85	4030
ethyl 4-aminobenzoate		4021	16		
	319	871	15	0.11	868
		865	19		
	280	7260	32	1.92	7228
		7195	11		

* $t_{tabulated}$ (P=0.05) = 2.31 (n=6 for each line).

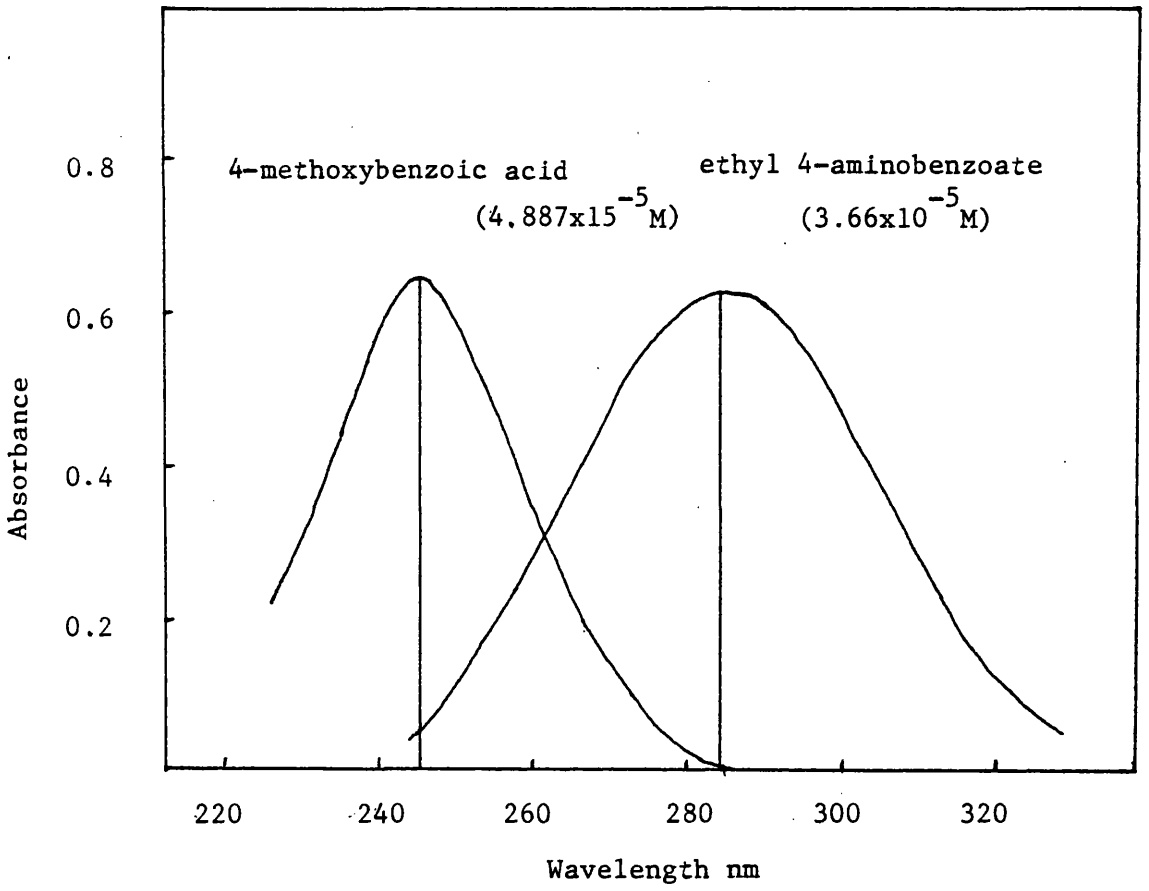


Figure 3.3 Absorption Spectra for Ethyl 4-aminobenzoate and 4-methoxybenzoic acid at pH 8.0 (ionic strength 1.0M).

Table 3.3 Spectrophotometric Data for the Ethyl 4-aminobenzoate : 4-methoxybenzoic acid Mixed Assay at pH 8.0 (ionic strength 1.0M).

Solute	Wavelength (nm)	Molar Extinction Coefficient	Standard Deviation	t_{calc}*	Mean Molar Extinction Coefficient
ethyl 4-aminobenzoate	285	17132 17275	133 161	0.68	17204
	246	2678 2684	36 26	0.14	2681
4-methoxybenzoic acid	285	237 240	10 5	0.27	239
	246	13450 13206	150 78	1.44	13328

* $t_{tabulated\ (P=0.05)} =$ 2.31 (n=6 for all times).

spectra was achieved together with a high sensitivity. Special precautions were, however, necessary as ethyl 4-aminobenzoate was present in an unionised species fraction of approximately 38%. As a pH change of 0.05% would introduce a 7% error into the assay it was essential that both the pH and ionic strength of the analytical solutions were carefully controlled. The ionic strength of both the experimental and analytical buffer solutions was 0.5 M, no further steps were therefore necessary to control the ionic strength. The pH of the analytical buffer solution was adjusted to 2.32 using small volumes of concentrated acid or alkali solution as required. Two replicate calibration curves obtained under these conditions were not significantly different at the 95% level of significance.

The second and simpler mixed assay (Case 2, figure 3.1) arises where the absorbance of one component is zero at the wavelength of maximum absorption of the other. The analytical method again involves experimental determination of the composite absorbance at two wavelengths, however, the two concentrations may be calculated independently instead of using simultaneous equations.

$$\text{Abs}_{\lambda a} = E^{A}_{\lambda a} \times C^{A} \times 1 \quad \text{.....(3.4)}$$

$$\text{Abs}_{\lambda b} = (E^{A}_{\lambda b} \times c^{A} + E^{B}_{\lambda b} \times C^{B}) .1 \quad \text{.....(3.5)}$$

The values of C^{A} can be calculated from equation (3.4) directly, as there is no interference from component B at the wavelength of maximum absorption of component A. If C^{A} is known, all constants in equation 3.5 are available to calculate the remaining variable, C^{B}. The assay of 4-nitrophenol in the presence of phenol and

4-methoxybenzoic acid were both examples of case 2 type mixed spectra. Details of spectra and extinction coefficient data are given in figure 3.4 and table 3.4 and figure 3.5 and table 3.5 respectively. The use of the Beer-Lambert relationship to estimate the concentration of two species in mixed solution assumes that the composite spectrum arises from the arithmetic sum of the individual spectra. It is important that the additive nature of the Beer-Lambert relationship is established for a particular binary system, using test solutions, prior to routine use. The absorbance of binary solutions of known composition was measured and the data submitted to a multiple linear regression analysis, based on equation 3.2 (Appendix 1). The molar extinction coefficient values estimated from the multiple linear regression analysis were compared with single solute data using a t-test. The results of this investigation are summarised in table 3.6. In all cases the calculated value of t did not exceed the tabulated value at the 95% level of significance. The mixed Beer-Lambert analytical determination of binary mixed solutions was therefore considered satisfactory for the systems used in this study.

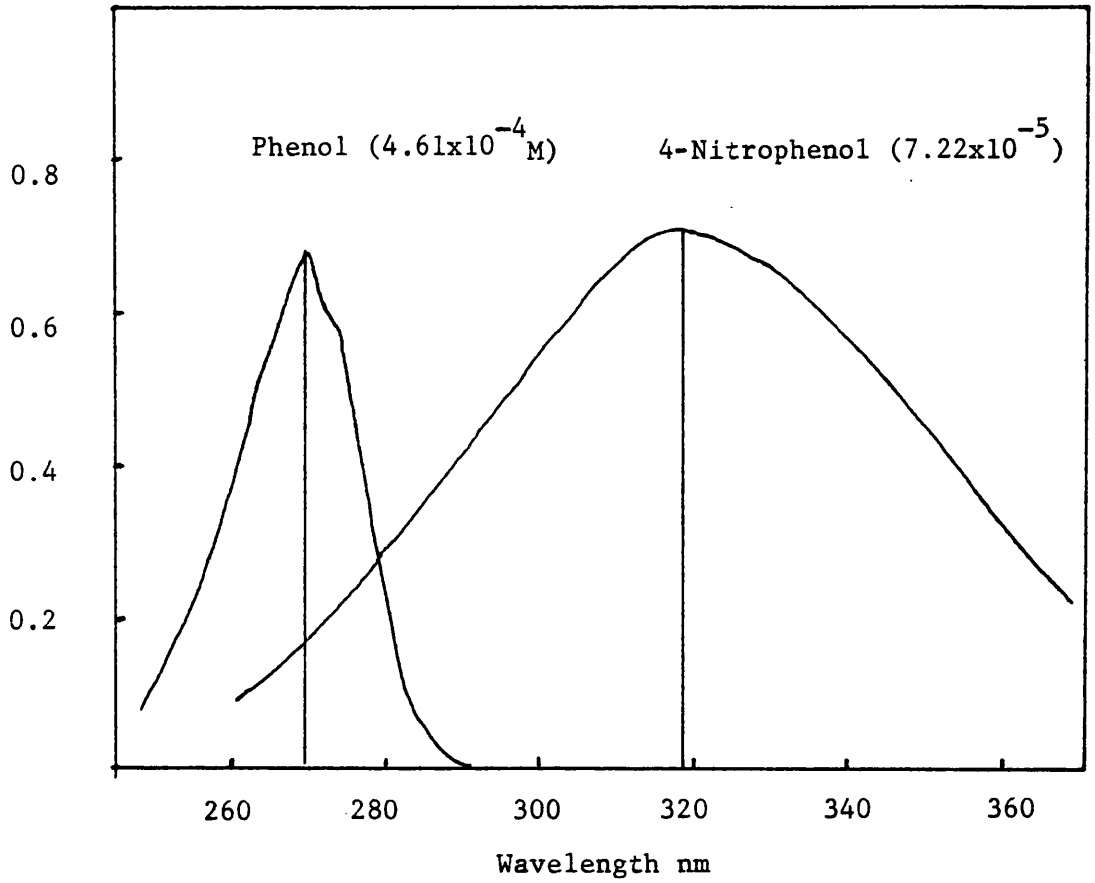


Figure 3.4 Absorption Spectra for Phenol and 4-Nitrophenol at pH 2.32 (0.5M ionic strength).

Table 3.4 Spectrophotometric Data for Phenol : 4-Nitophenol Mixed Assay at pH 2.32.

Solute	Wavelength (nm)	Molar Extinction Coefficient	Standard Deviation	t_{calc}*	Mean Molar Extinction Coefficient
4-nitrophenol	319	9857	68	0.43	9835
		9812	79		
	270	2444	31	0.31	2436
		2428	42		
phenol	319	No Absorbance			
	270	1476	20	0.04	1475
		1474	42		

* $t_{tabulated\ (P=0.05)} =$ 2.31 (n=6 for both lines).

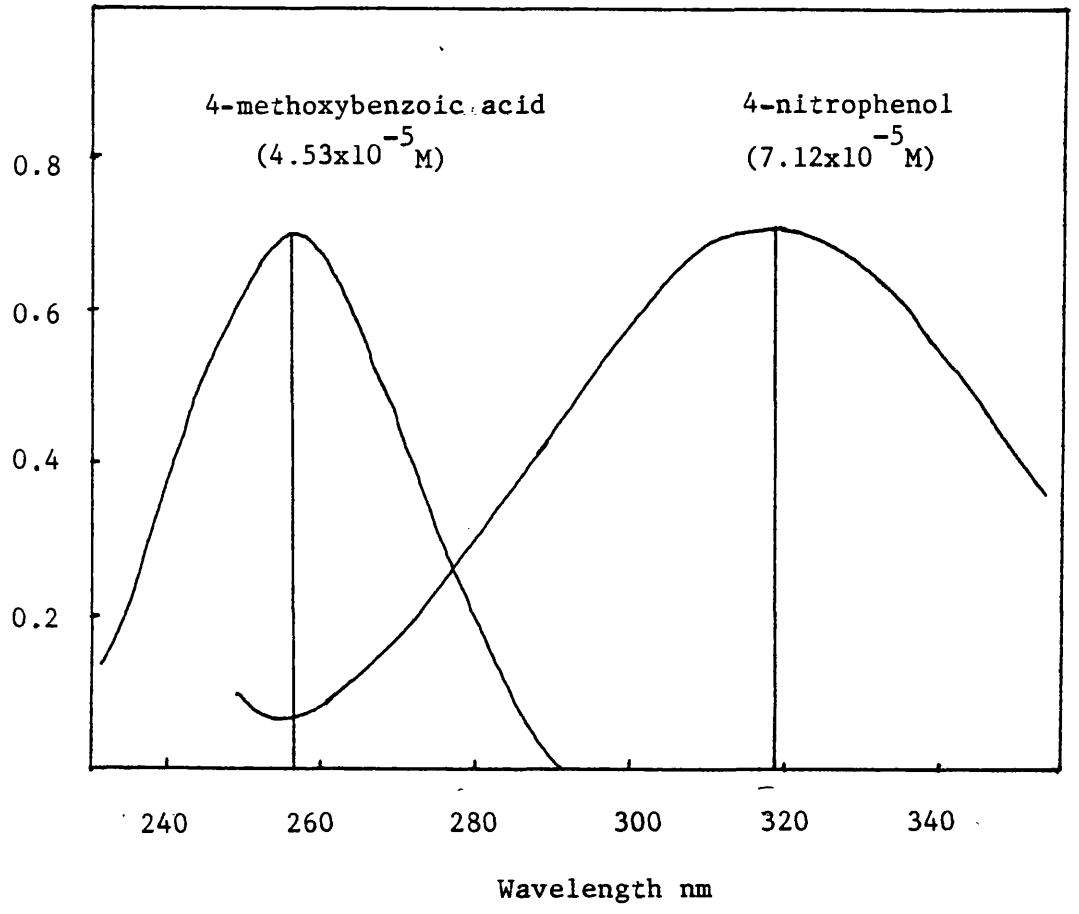


Figure 3.5 Absorption Spectra for 4-methoxybenzoic acid : 4-nitrophenol Mixed Assay at pH 2.32 (0.5M ionic strength).

Table 3.5 Spectrophotometric Data for 4-methoxybenzoic acid : 4-nitrophenol Mixed Assay at pH 2.32 (0.5M ionic strength).

Solute	Wavelength (nm)	Molar Extinction Coefficient	Standard Deviation	t_{calc}*	Mean Molar Extinction Coefficient
4-nitrophenol	319	9857 9812	68 79	0.43	9835
4-nitrophenol	256.5	1177 1174	5	0.51	1176
4-methoxybenzoic acid	319	No Absorbance			
4-methoxybenzoic acid	256.5	15525 15368	52 55	2.07	15447

* $t_{tabulated\ (P=0.05)} =$ 2.31 (n=6 for both lines).

Table 3.6 : Spectrophotometric Data for the Four Model Solutes Determined from Single Solute and Binary Solute Solution

Solute Species		Analytical Wavelength	Molar Extinction Coefficient						$t^{*}_{P=0.05}$
A	B		A Binary	A Single	B Binary	B Single	A_{calc}	B_{calc}	tab
4-methoxy-benzoic acid	ethyl 4-amino-benzoate	246	13420 (100)**	13228(114)	2705(22)	2681(30)	0.29	0.65	2.31
4-methoxy benzoic acid	4-nitrophenol	256.5	15529 (200)	15447(54)	1161(9)	1176(4)	0.16	1.52	2.31
ethyl 4-amino-benzoate	4-methoxy-benzoic acid	285	17155 (117)	17204(147)	230(11)	239(8)	1.07	0.66	2.31
ethyl 4-amino benzoate	4-nitrophenol	280	7233 (45)	7228(22)	3998(14)	4030(15)	0.10	1.56	2.31
4-nitrophenol	ethyl 4-amino-benzoate	319	9779 (15)	9835(40)	874(20)	868(17)	0.99	0.23	2.31
4-nitrophenol	phenol	270	2449 (25)	2436 (37)	1480(22)	1475(31)	0.10	0.13	2.31

* The t value is calculated from a comparison of the molar extinction coefficient determined from single and binary solute solution.

** Figures in brackets refer to the standard deviation of the molar extinction coefficient values

3.2 THE SORPTION OF MODEL SOLUTES BY NYLON 6 POWDER

3.2.1 Standard Procedure for the Determination of Sorption from Dilute Aqueous Solution.

A standard technique was employed to enable equilibrium of solution with nylon 6 powder and sampling to be carried out under isothermal conditions (Richardson 1973). Samples of nylon 6 powder were accurately weighed into tared 50ml conical flasks fitted with ground glass flanges to accept glass stoppers. The weight of powder used varied from 20 to 200mg depending upon the range of adsorbate uptake being investigated. A 10ml volume of single solute or binary solute solution was accurately pipetted into the flask which was then sealed by fitting the glass stopper. The flask was then shaken horizontally in a thermostatted shaking water bath at 7 cycles per minute until equilibrium was attained. The ground glass faces were lubricated with Apiezon T grease to ensure that a water-tight seal was achieved. The flask was submerged in the bath to a depth level with the centre of the stopper. This prevented evaporation of solvent from the surface of the solution followed by subsequent condensation on the upper portion of the flask, which would have effectively increased the solution concentration. At equilibrium, samples of the supernatant solution were withdrawn for spectrophotometric assay using a glass tube closed at one end with a number 3 size sintered glass filter disc. Samples were rapidly withdrawn by applying suction to the filter tube which were then transferred to 10ml volumetric flasks to equilibrate to ambient temperature before dilution with the appropriate analytical buffer prior to assay. A control flask was included in each

experimental batch of flasks, consisting of an appropriate weight of nylon 6 powder suspended in buffer solution without adsorbate. The control flask was set up, sampled and assayed using the standard technique. In all cases the control flask confirmed that no ultra violet absorbing species were leached from the polymer which would give rise to errors in the assay. Values of uptake were calculated using equation 1.1.

3.2.2 Equilibration Times.

Confirmation of the attainment of equilibrium is essential as the analysis of sorption data is carried out on the basis that the system is at equilibrium. Flasks containing the appropriate weight of nylon 6 powder, used for a particular system, and 10ml of solution were shaken at 30^{o} for varying time intervals under standard conditions before assay. The uptake of adsorbate on to nylon 6 powder as a function of time is shown in table 3.7. The results given in table 3.7 are the mean values of replicate determinations using 60 mesh nylon 6 powder. In all cases, maximum uptake occurred within one hour. Shaking times were, therefore, in excess of two hours to ensure that equilibrium had been established. The equilibrium time was redetermined for each change in experimental conditions, for both single solute and binary solute solutions, and the minimum two hour shaking time was in all cases found to be adequate.

Table 3.7 Uptake* of Adsorbates as a Function of Time by Nylon 6 Powder
Ionic Strength 0.5M at 30°

Time hours		ethyl 4-amino benzoate	ethyl 4-amino benzoate	4-methoxy-benzoic acid	4-nitrophenol	phenol
	Solvent	aqueous	buffer pH 3.44	buffer pH 3.44	buffer pH 2.32	buffer pH 2.32
1.0		8.08×10^{-2}	1.58×10^{-2}	1.88×10^{-2}	2.20	3.41
4.0		8.11×10^{-2}	1.58×10^{-2}	1.89×10^{-2}	2.17	3.42
8.0		8.07×10^{-2}	1.57×10^{-2}	1.89×10^{-2}	2.15	3.42
16.0		8.07×10^{-2}	1.58×10^{-2}	1.85×10^{-2}	2.18	3.43
24.0		8.07×10^{-2}	1.61×10^{-2}	1.86×10^{-2}	2.17	3.41
48.0		8.05×10^{-2}	1.57×10^{-2}	1.86×10^{-2}	2.20	3.42
nominal powder weight (g)		0.2	0.2	0.2	0.02	0.04
solution volume (ml)		10.0	10.0	10.0	10.0	10.0
Initial concentration (M)		6.028×10^{-3}	1.000×10^{-3}	1.018×10^{-3}	5.999×10^{-2}	0.306

* Unit : mol Kg^{-1}

3.2.3 Characterisation of the Sorption Isotherm.

The sorption isotherm for ethyl 4-aminobenzoate in aqueous solution was used to establish the reproducibility of the standard procedure and also to study the effects of altering the sample weight and particle size of sorbent in the system. Two flasks were set up for each initial concentration and a maximum difference of 2% was allowed for replicate values of the uptake. If the difference in uptake exceeded this limit, the supernatant solutions were re-assayed and if precision was not improved the whole determination was repeated. This procedure was carried out for all nylon 6 isotherm determinations described subsequently. Two replicate isotherms were determined for the sorption of ethyl 4-aminobenzoate from aqueous solution using 200 mg of 60 mesh nylon 6 powder. In addition, isotherms were determined using 100 and 400 mg of this sorbent. To study the effect of particle size, two replicate sorption isotherms were determined using 200 mg of sorbent and particle size fractions corresponding to >60 mesh, 60 - 120 mesh and <120 mesh sieve diameters.

Treatment of Results.

Typical data for the sorption of ethyl 4-aminobenzoate are given in table 3.8 and the sorption isotherms for uptake on to 200 and 400 mg of sorbent over the concentration range 0 - 6 x 10^{-3}M are shown in figure 3.6. The isotherm is linear and may be described as a C_1 type according to Giles' classification. The data for this isotherm determination was analysed by a computerised linear least-squares regression program and the slopes (K values) and intercepts together with other associated statistical data are summarised in tables 3.9 and 3.10.

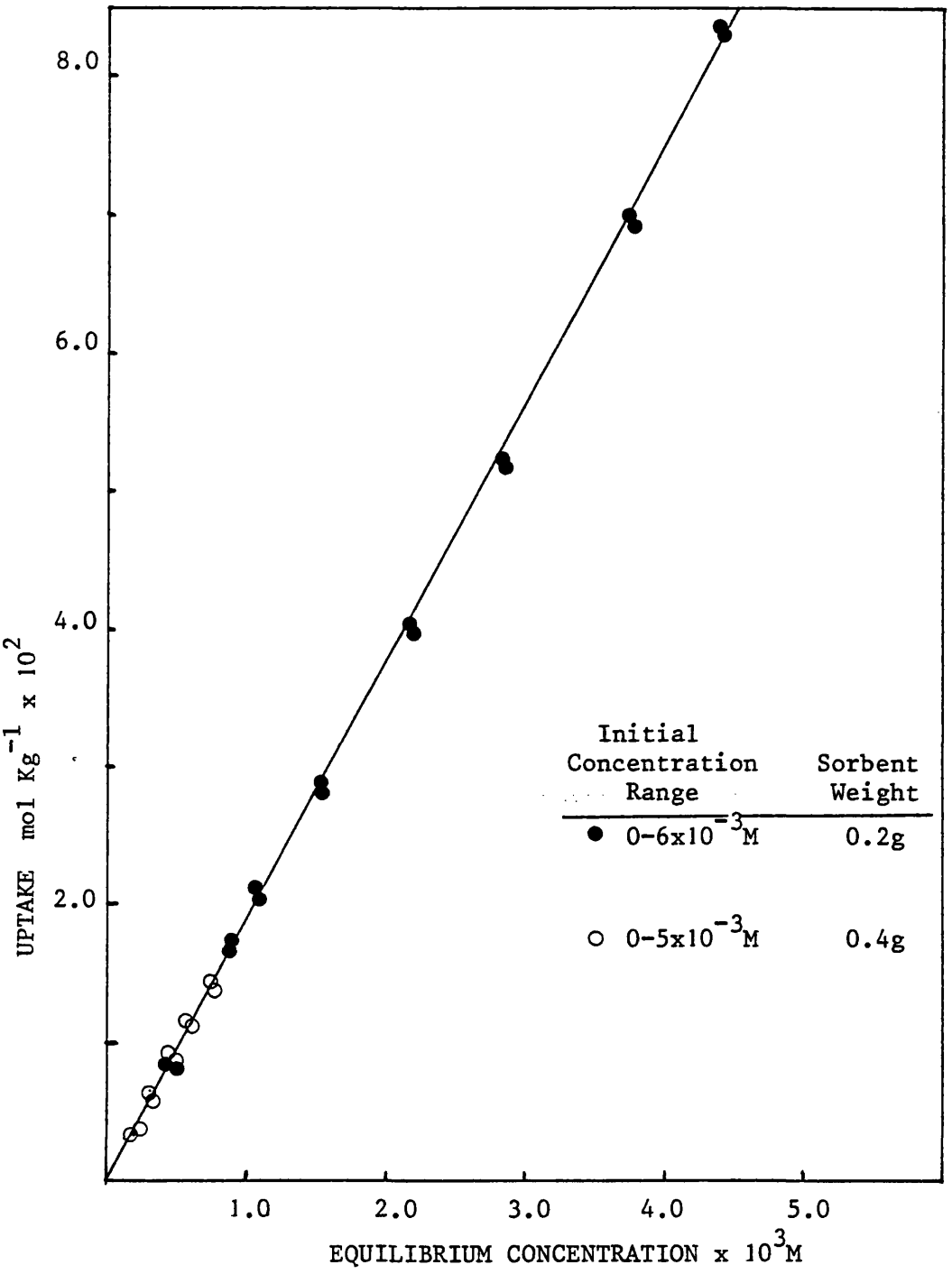


FIG 3.6 SORPTION ISOTHERM OF ETHYL 4-AMINOBENZOATE BY 60 MESH NYLON 6 POWDER FROM AQUEOUS SOLUTION AT 30°

Table 3.8 Data for the Sorption Isotherm of Ethyl 4-Aminobenzoate by 60 Mesh Nylon 6 Powder From Simple Aqueous Solution at 30°. (Initial Concentration Range 0 - 6 x 10^{-3} M).

Initial Concentration x 10^4M	Equilibrium Concentration x 10^4M	Weight of Sorbent (grammes)	Uptake mol Kg^{-1}
2.061	1.421	0.200	0.0032
	1.415	0.200	0.0032
4.108	2.936	0.300	0.0059
	2.869	0.200	0.0063
6.150	4.430	0.200	0.0086
	4.460	0.200	0.0084
6.169	4.352	0.200	0.0091
	4.250	0.200	0.0091
8.126	5.803	0.200	0.0116
	5.803	0.200	0.0116
10.19	7.325	0.200	0.0143
	7.325	0.200	0.0143
12.31	8.961	0.200	0.0167
	8.873	0.200	0.0173
15.10	11.00	0.201	0.0204
	10.90	0.200	0.0210
21.17	15.57	0.200	0.0280
	15.53	0.200	0.0282
30.00	22.00	0.200	0.0401
	22.00	0.200	0.0401
38.96	28.62	0.200	0.0516
	28.66	0.200	0.0516
51.54	37.60	0.200	0.0697
	37.72	0.200	0.0690
60.80	44.00	0.202	0.0834
	44.00	0.202	0.0834

Discussion of Results.

The isotherm data all show high linear correlation coefficents and in most cases the intercepts spanned the origin within two standard deviations. In several cases, however, the intercepts were outside the limit of two standard deviations from the origin although the value of the intercept was numerically small compared to the lowest value of uptake. The isotherms were considered to be C_1 type in nature although not fulfiling the criteria of

Table 3.9 Statistical Data for Replicate Isotherm Determinations of Ethyl 4-aminobenzoate onto 60 Mesh Nylon 6 Powder from Aqueous Solution at 30°.

Concentration Range/Sorbent weight	K_1 Kg^{-1}	Standard Deviation	Intercept mol Kg^{-1} x 10^4	Standard Deviation x 10^4	Correlation Coefficient
0 - 6 x 10^{-3}M 0.2 gramme	18.6	0.2	- 1.75	3.85	0.999
0 - 1 x 10^{-3}M 0.2 gramme	18.2	0.2	3.86	6.24	0.999
0 - 5 x 10^{-3}M 0.1 gramme	18.1	0.2	6.31	2.84	0.999
0 - 5 x 10^{-3}M 0.4 gramme	19.4	0.3	3.06	1.34	0.999
Analysis of variance - $F_{calc} = 0.02$ $F_{tab\ 3,38} = 2.88$ (P = 0.05)					

Richardson (1973) which is discussed in Section 4.1.2.1.1. Linear isotherms can be characterised by their slope, or K value, as the uptake of the solute is directly proportional to the equilibrium concentration. For all other interaction systems where C_1 type linearity was found, only the K values and intercepts, together with their associated standard deviations and the correlation coefficient are subsequently quoted in the text.

Comparison of the K values for the sorption of ethyl 4-aminobenzoate over the range 0 - 5 x 10^{-3} M initial concentration using 0.2 gramme of 60 mesh nylon 6 powder (table 3.9) showed them to be not significantly different ($t_{calculated}$ = 1.41, $t_{tabulated}$ = 2.04 $n_1 + n_2 = 36$, P = 0.05). Table 3.9 also shows that sorbent weight does not influence sorption as the slopes (K values) for 0.1 gramme, 0.2 gramme and 0.4 gramme, 60 mesh nylon 6 powder using an F test (Appendix 1) were also not significantly different. Similarly, the data in table 3.10 indicates that there is no significant difference in the K values using sorbent particles of > 60, 60 - 120 and < 120 sieve size. The > 60 mesh size fraction of nylon 6 powder was therefore used for all subsequent sorption experiments. The mean value of K in tables 3.9 and 3.10 was 18.73 1 Kg^{-1} which is close to that of 19.43 1 Kg^{-1} obtained for the sorption of ethyl 4-aminobenzoate from unbuffered aqueous solution containing no added electrolyte by Richardson (1973).

Table 3.10 Statistical Data for the Sorption of Ethyl 4-aminobenzoate From Aqueous Solution on to Nylon 6 Powder of Different Particle Sizes at 30° (Initial Concentration Range 0-5 x 10^{-3} M).

Sieve Size	K $l\ Kg^{-1}$	Standard Deviation	Intercept $mol\ Kg^{-1}$ x 10^{4}	Standard Deviation x 10^{4}	Correlation Coefficient
60	18.7	0.3	-5.03	6.88	0.999
	18.5	0.3	5.75	8.04	0.999
60 - 120	18.5	0.3	15.75	7.47	0.999
	18.9	0.5	8.85	11.40	0.999
<120	19.1	0.6	12.01	18.02	0.998
	19.2	0.3	4.27	6.58	0.999
Analysis of Variance	$F_{calc} = 0.69$	$F_{tab\ 5,24} = 2.62$	(P = 0.05).		

3.2.4 The Sorption of Model Solutes from Single Solute Solution.

The sorption of phenol, 4-nitrophenol, ethyl 4-aminobenzoate and 4-methoxybenzoic acid was determined from constant ionic strength buffer (McIlvaine's citrate phosphate, 0.5M) at 30°. The pH of the systems used were selected to optimise the fraction of the solute in the unionised form present in binary solute solutions which were the subject of later studies (Section 3.2.5.1.1.).The sorption of phenol and 4-nitrophenol was studied at pH 2.32 and ethyl 4-aminobenzoate and 4-methoxybenzoic acid at pH 3.44. The sorption isotherms shown in figures 3.7 - 3.10 indicate that ethyl 4-aminobenzoate, 4-methoxybenzoic acid and phenol are of the C_1 type, over the concentration range studied, whereas that for 4-nitrophenol is of C_2 type. K values for the model compounds are given in Table 3.11, including that for 4-nitrophenol which was calculated from

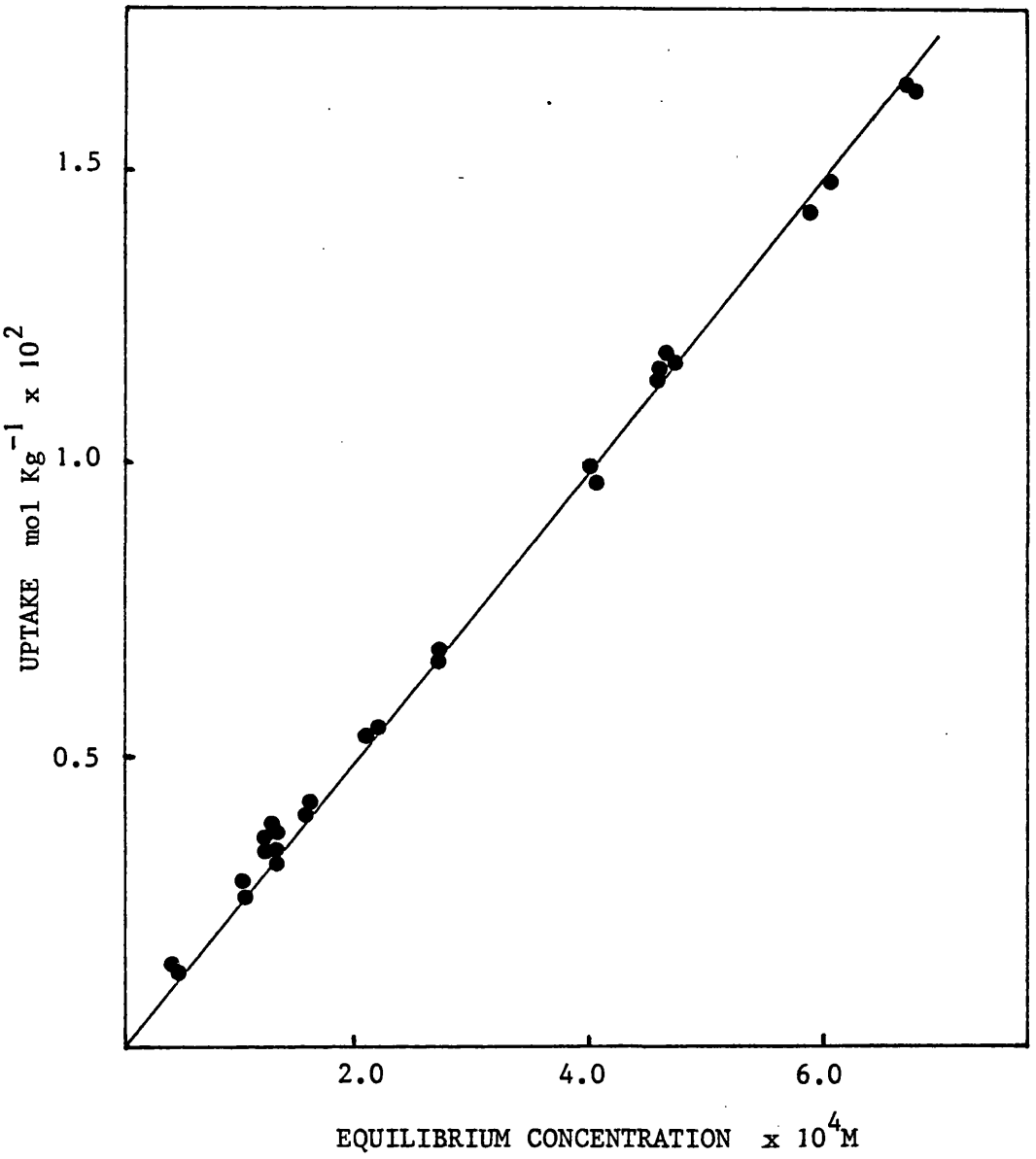


FIG 3.7 SORPTION ISOTHERM OF ETHYL 4-AMINOBENZOATE BY NYLON 6 POWDER FROM DILUTE SOLUTION AT pH 3.44(0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

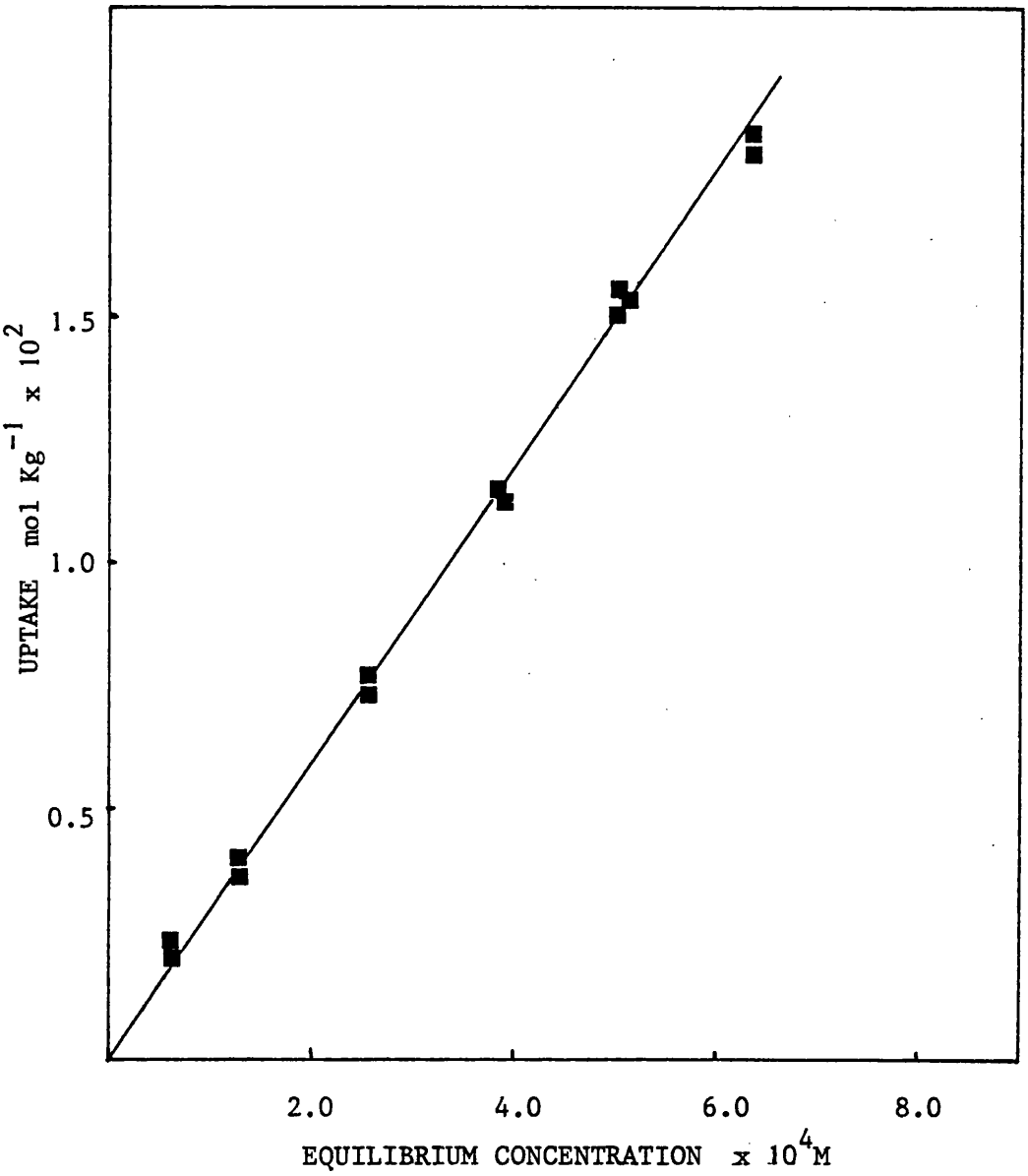


FIG 3.8 SORPTION ISOTHERM OF 4-METHOXYBENZOIC ACID BY NYLON 6 POWDER FROM DILUTE SOLUTION pH 3.44(0.5M IONIC STRENGTH) AT 30°. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

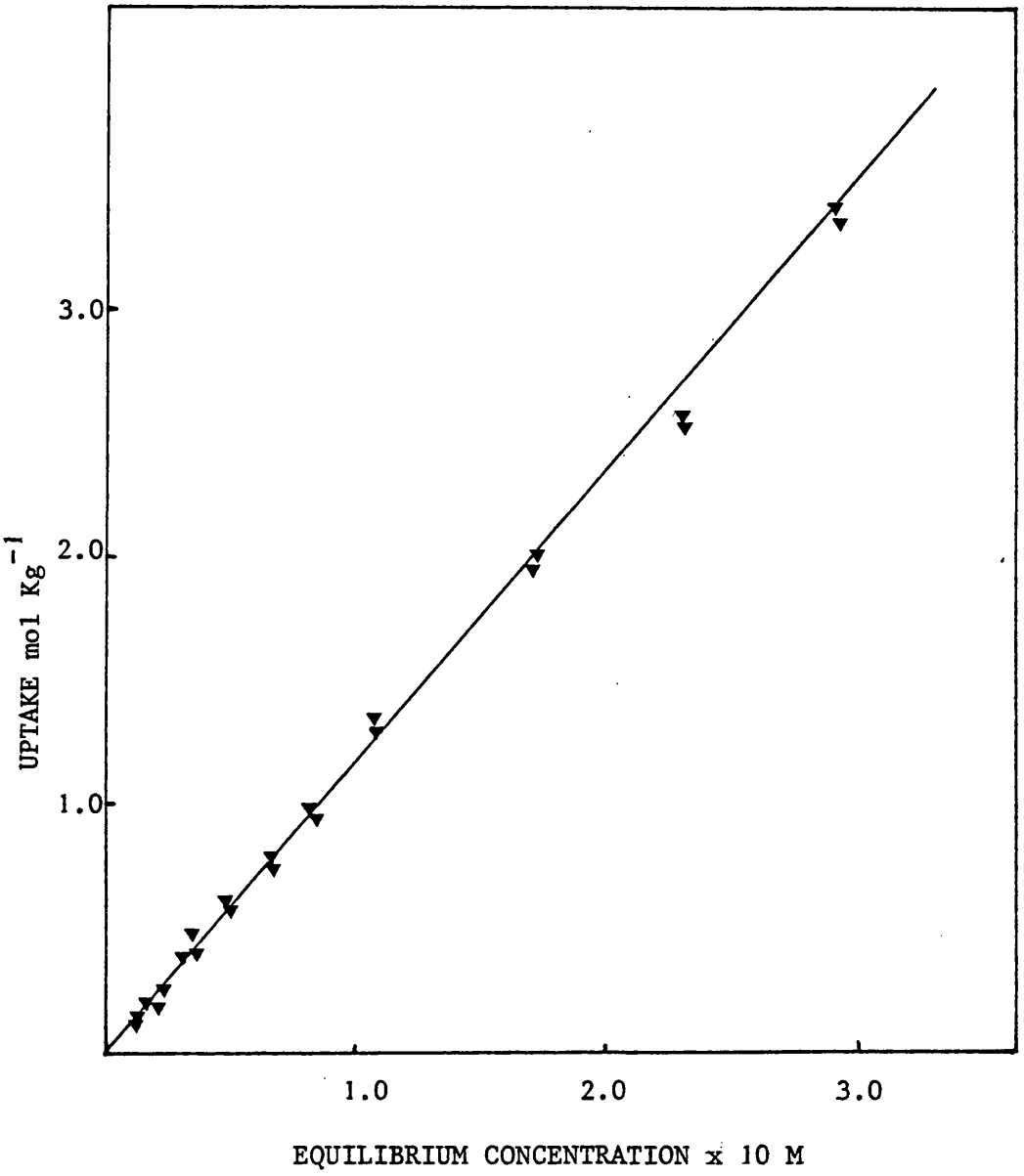


FIG 3.9 SORPTION ISOTHERM OF PHENOL BY NYLON 6 POWDER FROM DILUTE SOLUTION pH 2.32(0.5M IONIC STRENGTH) AND 30° INITIAL CONCENTRATION RANGE 0 - 0.3M

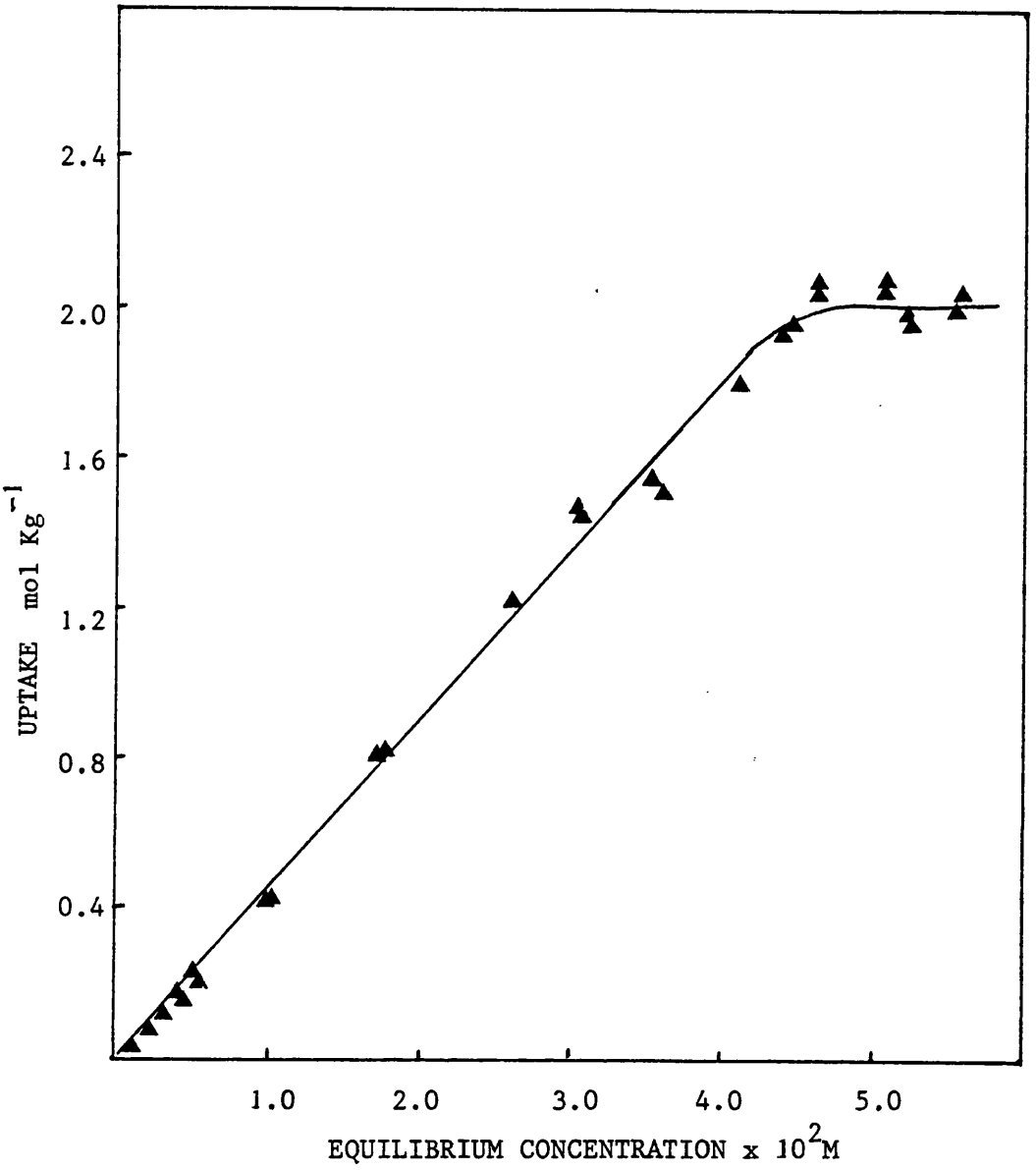


FIG 3.10 SORPTION ISOTHERM OF 4-NITROPHENOL BY NYLON 6 POWDER FROM DILUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o}. INITIAL CONCENTRATION RANGE 0 - 6 x 10^{-2}M

data in the linear C_1 region of the isotherm. As the nature of the 4-nitrophenol isotherm is clearly not comprehensively represented by the K value the experimental data are included in Table 3.12.

Table 3.11 Sorption Isotherm Data for Phenol 4-nitrophenol 4-methoxybenzoic acid and Ethyl 4-aminobenzoate from Dilute Aqueous Solution at 30° and Ionic Strength 0.5M.

Compound	pH	K $1\ Kg^{-1}$	Standard Deviation	Intercept $mol\ Kg^{-1} \times 10^4$	Standard Deviation $\times 10^4$	Correlation Coefficient
ethyl 4-amino-benzoate	3.44	22.3	0.6	4.24	2.75	0.999
4-methoxy benzoic acid	3.44	28.1	0.8	3.47	3.38	0.997
phenol	2.32	11.6	0.3	5.2	5.70	0.998
4-nitro-phenol *	2.32	42.3	0.9	3.83	2.57	0.998

* K value determined from C_1 region of the sorption isotherm (Fig.3.10).

3.2.4.1 Determination of the Desorption Isotherm.

The reversible nature of the binding of benzoic acid derivatives by nylon 6 powder has been established previously (Richardson 1973). Desorption data was therefore only determined for the interaction of nylon 6 with the two phenolic solutes. Sorption isotherms for phenol and 4-nitrophenol (in the C_1 region of the isotherm) were determined using the standard method described in Section 3.2.1. At equilibrium, exactly 5 ml of the supernatant was removed for assay, and 5 ml of buffer solution was then added to replace the sample.

Table 3.12 Data for the Sorption Isotherm of 4-nitrophenol by Nylon 6 Powder from Dilute Solution pH 2.32 (0.5M ionic strength) and 30°.

Initial Concentration $M \times 10^2$	Equilibrium Concentration $M \times 10^2$	Weight gramme	Uptake $mol\ kg^{-1}$
1.20	1.03	0.0401	0.42
	1.03	0.0399	0.42
1.31	0.88	0.100	0.42
	0.89	0.101	0.41
2.54	1.74	0.100	0.81
	1.73	0.101	0.80
3.67	3.07	0.402	1.49
	3.09	0.0401	1.45
3.86	2.65	0.101	1.20
	2.62	0.101	1.23
4.83	4.12	0.0401	1.77
	4.11	0.0402	1.80
5.07	4.63	0.0195	2.08
	4.66	0.0196	2.08
5.14	3.62	0.099	1.52
	3.58	0.100	1.55
5.49	5.07	0.0200	2.09
	5.07	0.0203	2.05
5.98	5.20	0.0398	1.97
	5.20	0.0399	1.96
5.99	5.59	0.0197	2.02
	5.58	0.0198	2.06
6.40	4.48	0.100	1.91
	4.48	0.100	1.91

The buffer solution was returned via the same sintered glass filter tube to ensure that all nylon 6 powder, adhering to the filter in the course of sampling was washed back into the flask to minimise loss of powder weight. The system was then allowed to reequilibrate and was resampled using the standard procedure. The sorption and desorption isotherms were both linear C_1 type for these compounds; K values for the sorption and desorption isotherms are given in table 3.13. Comparison of the K values using the t-test for similar

Table 3.13 Sorption and Desorption Isotherms for Phenol and 4-nitrophenol by Nylon 6 Powder from Dilute Solution pH 2.32 (ionic Strength) 0.5M at 30^{o} Initial Concentration Range 0 - 5 x 10^{-3}M.

Adsorbate	Isotherm	K L Kg^{-1}	Standard Deviation of K	t_{calc} P=0.05	Intercept mol Kg^{-1} x10^{4}	Standard Deviation of Intercept x 10^{4}	Correlation Coefficient
4-nitrophenol	sorption	42.3	0.3	0.80	3.83	2.57	0.998
4-nitrophenol	desorption	41.9	0.4		4.01	5.31	0.997
phenol	sorption	11.6	0.3	1.71	5.20	5.70	0.998
phenol	desorption	10.6	0.5		6.01	7.00	0.998

t_{tab} = 2.09, n=12 for all isotherms

slopes confirms that no significant difference exists between the sorption and desorption isotherms at the 95% level of significance (table 3.13). The binding of phenol and 4-nitrophenol by nylon 6 was therefore, considered to be fully reversible.

3.2.5. Sorption Isotherms from Binary Solute Solutions.

Isotherms for the four model solutes were determined from binary mixed solution using the standard experimental procedure. The binary systems used are identified in terms of the ratios of their initial concentrations. The system of nomenclature adopted is a statement of the two adsorbate species, followed by their respective initial concentraion molar ratio in parentheses. Thus a phenol : 4-nitrophenol (5:1) system represents a solution where the initial molar concentration of phenol is 5 times that of 4-nitrophenol. This system gives an indication of the relative species concentrations within the stated concentration range. The solutions used for the isotherm experiments were formulated by diluting a stock mixture of specified initial concentration ratio with buffer.

The sorption study from binary mixed solution was carried out in two stages. Firstly, mixed systems composed of ethyl 4-amino-benzoate and 4-methoxybenzoic acid were studied to assess the nature of sorption from binary solute solution, and the physico-chemical factors affecting the resulting equilibria. Secondly, mixed systems composed of phenolic and benzoic acid derivatives were studied to assess the effect of solute chemical structure on the sorption behaviour from binary solute solution.

3.2.5.1.1 The Uptake of Ethyl 4-aminobenzoate and 4-methoxybenzoic Acid from Binary Solute Solution by Nylon 6 Powder.

The extent of sorption of a weak aromatic electrolyte by nylon 6 is proportional to the fraction of the solute present in the unionised form (Richardson 1973). Sorption from mixtures of ethyl 4-aminobenzoate and 4-methoxybenzoic acid were therefore carried out at pH 3.44 which results in these compounds being approximately 91% and 88% undissociated respectively. Sorption isotherms for ethyl 4-aminobenzoate in the presence of 4-methoxybenzoic acid were determined in intial concentration ratios of 5:1, 1:1, and 1:5. Sorption isotherms are shown plotted in figures 3.11 and 3.12 where it can be seen that all isotherms are C_1 type and can therefore be represented by the K value. These are given in table 3.14 which includes the single solute isotherm data taken from table 3.11 for comparison.

The data in table 3.14 shows that there is no significant difference between the sorption characteristics of ethyl 4-aminobenzoate or 4-methoxybenzoic acid when taken up from single solute or binary solute solution as in all cases the tabulated t value at the 95% level of significance exceeds the calculated value.

3.2.5.1.2 Determination of the Desorption Isotherms.

After determining the sorption isotherms for 4-methoxybenzoic acid and ethyl 4-aminobenzoate from the 1:1 mixture, their desorption isotherms were determined using the procedure outlined in section 3.2.2. The desorption isotherms were also linear and not significantly different from the sorption isotherms (table 3.15) for this mixture of solutes.

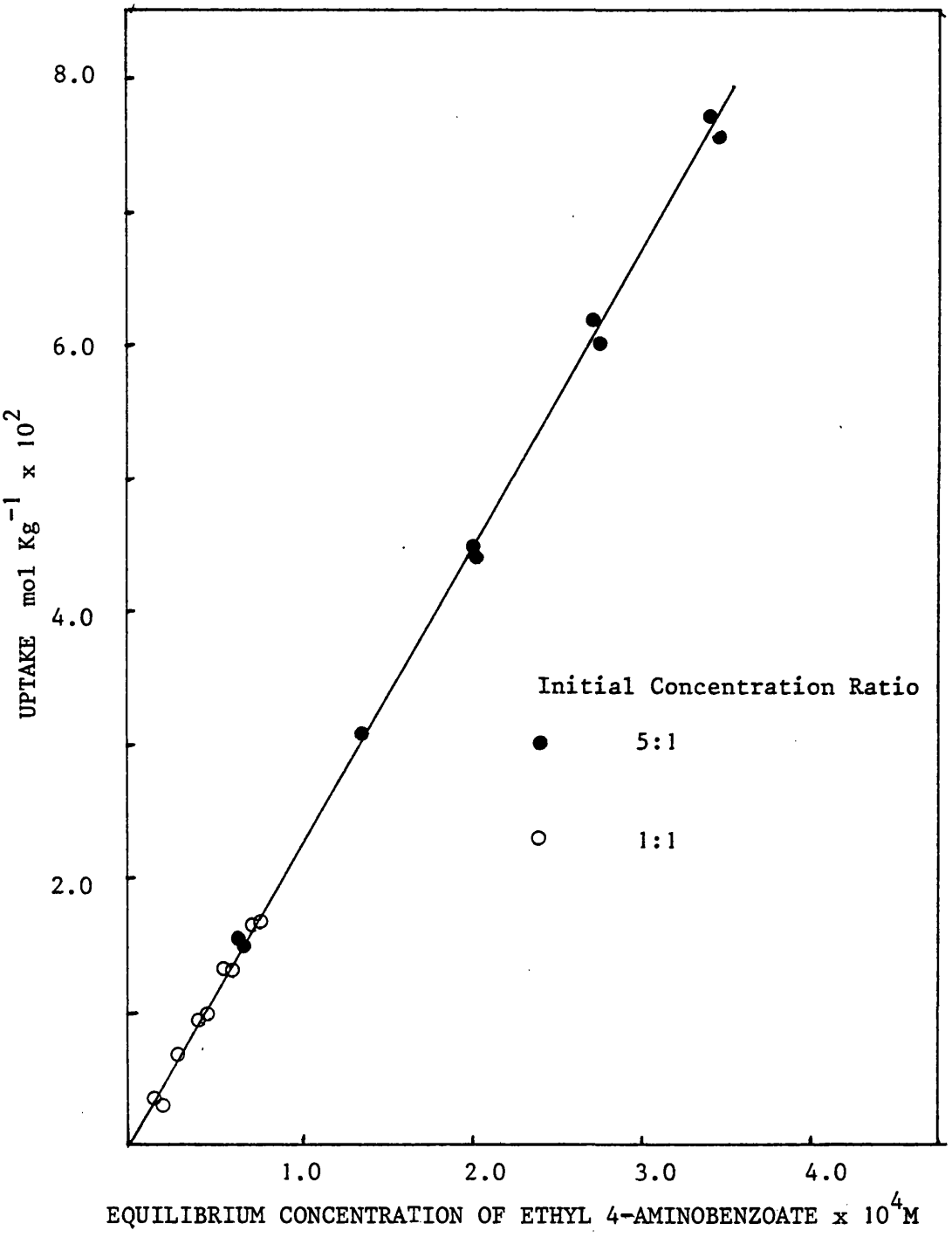


FIG 3.11 SORPTION ISOTHERMS OF ETHYL 4-AMINOBENZOATE BY NYLON 6 POWDER FROM ETHYL 4-AMINOBENZOATE:4-METHOXYBENZOIC ACID (1:1) AND (5:1) INITIAL CONCENTRATION RATIO MIXED SOLUTIONS AT pH 3.44 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGES: ETHYL 4-AMINOBENZOATE - 0 - 10^{-3}M AND 0 - 5 x 10^{-3}M AND 4-METHOXYBENZOIC ACID, 0 - 10^{-3}M.

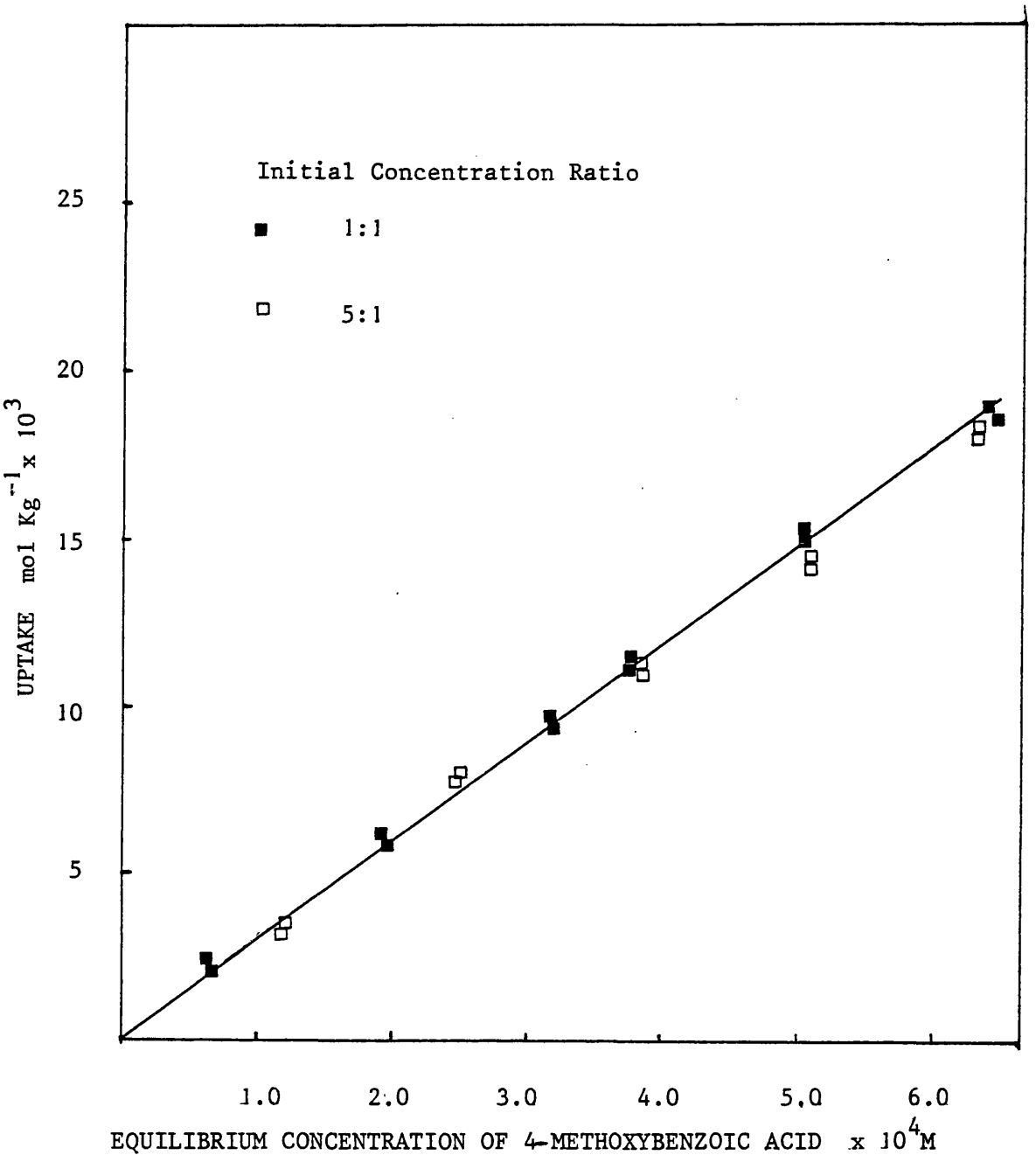


FIG 3.12 SORPTION ISOTHERMS OF 4-METHOXYBENZOIC ACID BY NYLON 6 POWDER FROM ETHYL 4-AMINOBENZOATE:4-METHOXYBENZOIC ACID (1:1) AND (5:1) INITIAL CONCENTRATION RATIO MIXED SOLUTIONS AT pH 3.44 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGES: ETHYL 4-AMINOBENZOATE, 0 - 10^{-3}M AND 0 - 5 x 10^{-3}M AND 4-METHOXYBENZOIC ACID, 0 - 10^{-3}M

Table 3.14 Isotherm Data for the Sorption of Ethyl 4-aminobenzoate and 4-methoxybenzoic acid on to Nylon 6 Powder from Ethyl 4-aminobenzoate : 4-methoxybenzoic acid (1:1), (5:1) Mixed Solutions and Single Solute Solution at pH 3.44 (0.5M ionic strength) and 30°.

Initial Concentration Range : ethyl 4-aminobenzoate :0-5 x 10^{-3} M.

Adsorbate	Ethyl 4-Aminobenzoate : 4-Methoxybenzoic Acid Initial Concentration Ratio		K 1 Kg^{-1}	Standard Deviation of K	t**		Intercept mol Kg^{-1} x10^{4}	Standard Deviation x 10^{4}	Correlation Coefficient
					calc	tab			
ethyl 4-aminobenzoate	(10)*	1:0	22.3	0.6	-		4.24	2.76	0.998
ethyl 4-aminobenzoate	(12)	1:1	23.2	0.4	1.25	2.10	2.41	1.65	0.997
ethyl 4-aminobenzoate	(10)	5:1	21.9	0.3	0.59	2.12	1.36	6.08	0.999
4-methoxybenzoic acid	(10)	0:1	28.1	0.8	-		3.47	3.38	0.997
4-methoxybenzoic acid	(12)	1:1	28.9	0.6	0.80	2.10	3.25	2.38	0.997
4-methoxybenzoic acid	(10)	5:1	27.7	0.6	0.40	2.12	5.28	2.25	0.998

* Number of experimental data points on the isotherm.

** t_{calc} value comparing the isotherm K values determined from single solute and binary solute solution experiments.

Table 3.15 Sorption and Desorption Isotherms for ethyl 4-aminobenzoate and 4-methoxybenzoic acid and Nylon 6 Powder from an ethyl 4-aminobenzoate : 4-methoxybenzoic acid (1:1) Binary Mixed Solution at pH 3.44 (ionic strength) and 30°. Initial Concentration Range of Both Solutes 0 - 1 x 10^{-3}M.

Solute (isotherm)	$K_{1kg^{-1}}$		Standard Deviation of K	t		Intercept mol $Kg^{-1}_{x}10^{4}$	Standard Deviation of Intercept x 10^4	Correlation Coefficient
				tab	calc			
ethyl 4-amino-benzoate (sorption)	23.2	(10) *	0.4	0.83	2.12	2.41	1.65	0.997
ethyl 4-amino-benzoate (desorption)	22.6	(10)	0.6			1.93	1.86	0.999
4-methoxybenzoic acid (sorption)	28.9	(10)	0.6	0.70	2.12	3.25	2.38	0.997
4-methoxybenzoic acid (desorption)	29.6	(10)	0.8			1.48	4.42	0.997

* Number of experimental data points on the isotherm.

3.2.5.1.3. The Effect of pH

Sorption isotherms for 4-methoxybenzoic acid and ethyl 4-aminobenzoate were also determined using McIlvaine's buffer pH 2.32 (0.5M ionic strength). At this pH, 4-methoxybenzoic acid and ethyl 4-aminobenzoate are approximately 99% and 40% unionised respectively. Both isotherms at pH 2.32 were linear and the results of a computerised linear least-squares regression analysis of the experimental data for single solute and binary solute solution determination are shown in table 3.16. Isotherm data for the single and mixed solute interaction at pH 3.44 from table 3.14 are also included.

Comparison of K values using the standard t-test indicated that no significant difference exists between the single solute and binary solute isotherms at the 95% level of significance at either pH.

3.2.5.1.4 The Effect of Temperature.

The isotherms of ethyl 4-aminobenzoate and 4-methoxybenzoic acid from a(1.1)binary solution were determined at various temperatures over the range 15^{o} - 60^{o} using the standard experimental procedure. For comparison the isotherms for the two model solutes were also determined from single solute solutions over this temperature range. The pH of the solution was nominally set at 3.44 at 30^{o} and was found to vary between pH 3.42 at 15^{o} to 3.46 at 60^{o}, a difference of 1% over the temperature range studied. This temperature effect on pH was not considered to be of significance.

Treatment of results.

The sorption K value has been considered to be approximately equal to the thermodynamic equilibrium constant K' (Autian 1963, Richardson 1973). The temperature dependence of the equilibrium constant is given by the Van't Hoff Equation (equation 3.6).

Table 3.16 The Effect of pH on the Sorption of Ethyl 4-aminobenzoate and 4-methoxybenzoic acid on to Nylon 6 Powder from an Ethyl 4-aminobenzoate : 4-methoxybenzoic acid (1:1) Binary Mixed Solution Ionic Strength 0.5M at 30° Concentration range : 0 - 1 x 10^{-3} M for each Solute.

Solute	pH	K $l\ Kg^{-1}$	Standard Deviation of K	t statistic**		Intercept $mol\ Kg^{-1} \times 10^{4}$	Standard Deviation of Intercept $\times 10^{4}$	Correlation Coefficient
				calc	tab			
ethyl 4-amino- benzoate *	3.44	22.3	0.6	1.25	2.12	4.24	2.76	0.998
ethyl 4-amino- benzoate	3.44	23.2	0.4			2.41	1.65	0.997
ethyl 4-amino- benzoate *	2.32	9.9	0.3			8.51	1.40	0 997
4-methoxybenzoic acid *	3.44	28.1	0.8	0.80	2.12	3.47	3.38	0.997
4-methoxybenzoic acid	3.44	28.9	0.6			3.25	2.38	0.997
4-methoxybenzoic acid *	2.32	29.2	0.3	0.63	2.12	7.16	1.35	0.999
4-methoxybenzoic acid	2.32	28.6	0.9			2.21	4.04	0.996

* - single solute data included for comparison.

** All isotherms consisted of 10 data points.

$$\frac{d\ln K}{dt} = \frac{\Delta H^{o}}{RT^{2}} \quad \text{.....(3.6)}$$

where T = absolute temperature

ΔH^{o} = the standard enthalpy change associated with the overall sorption process.

R = the universal gas constant.

Integration of equation 3.6 assuming that ΔH^{o} remains constant over the temperature range of the integration leads to equation 3.7.

$$\log_{10}K = \frac{-\Delta H^{o}}{2.203R}\ \frac{1}{T} + \text{constant} \quad \text{.....(3.7).}$$

If ΔH^{o} is constant a linear plot of $\log_{10}K$ versus $^{1}/T$ will result, from which the standard enthalpy change can be calculated. Accurate estimates of ΔH^{o} are obtained by submitting the linear slope of this Van't Hoff plot, to a computerised linear least squares regression analysis.

If a standard state of unit molal concentration is adopted, an estimate of the standard free energy of sorption can be obtained from equation 3.8.

$$\Delta G^{o} = -R.T\ln K \quad \text{.....(3.8).}$$

where ΔG^{o} = this standard free energy change associated with the overall sorption process (standard state model concentration).

As ΔG^{o} and ΔH^{o} are known, ΔS^{o}, the standard entropy change for the overall sorption process follows from equation 3.9, the Gibbs equation.

$$\Delta G^{o} = \Delta H^{o} - T\ \Delta S^{o} \quad \text{.....(3.9).}$$

Van't Hoff isochores for the two solutes are shown plotted in figure 3.13 where a point of inflexion is apparent for both solutes at 40^{o}. The Van't Hoff data for the two solutes are given in tables 3.17 and 3.18, comparison of the K values for the single and binary solute systems at each temperature, using the standard t test, indicates that no significant difference exists between them at any temperature within the range studied. Thermodynamic parameters for the single and binary solute data are shown in table 3.19 where the two values of ΔH^{o} were calculated from the linear slopes on either side of the inflexion. An additional single solute isotherm for ethyl 4-aminobenzoate at 5^{o} cf table 3.17) was determined to improve the estimate of the ΔH^{o} value on the low temperature side of the point of inflexion in the isochore.

3.2.5.2. Uptake from Binary Solutions of 4-nitrophenol and Phenol by Nylon 6 Powder.

Sorption isotherms for phenol and 4-nitrophenol from single solute and binary solute solution were determined using the standard experimental procedure. All determinations were carried out at pH 2.32 (0.5M ionic strength) using McIlvaine's buffer. This pH was selected to ensure that both solutes were fully unionised, and to enable comparison with the ethyl 4-aminobenzoate and 4-methoxybenzoic acid systems also measured at pH 2.32.

Sorption isotherms for the uptake of phenol on to nylon 6 powder from phenol : 4-nitrophenol (1:1) and (3:1) binary solute solutions systems, together with its single solute isotherm, are shown in figure 3.14. The corresponding 4-nitrophenol isotherms are plotted in figure 3.15. The isotherms for phenol are linear

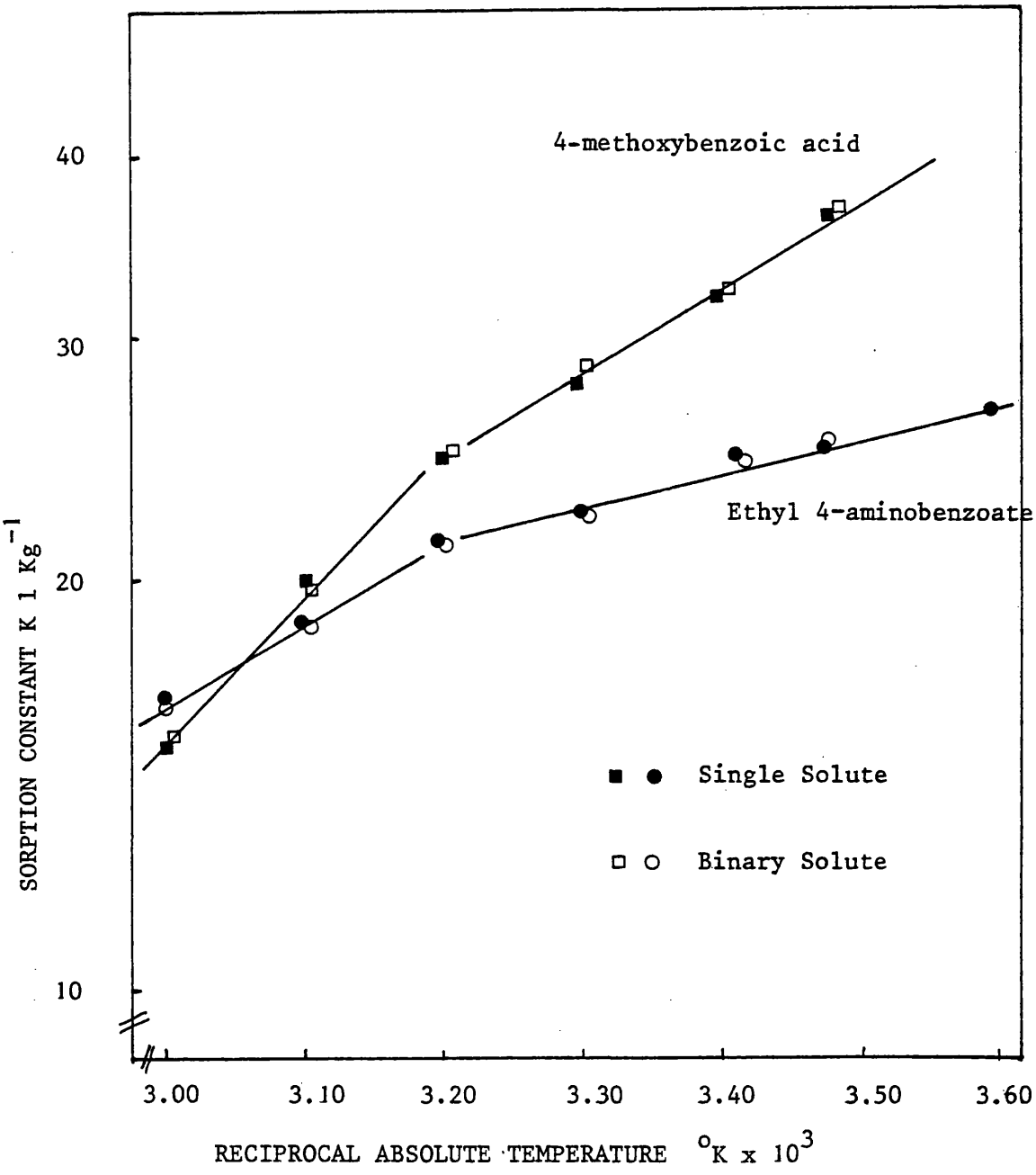


FIG 3.13 VAN'T HOFF ISOCHORES FOR THE EFFECT OF TEMPERATURE ON THE SORPTION OF ETHYL 4-AMINOBENZOATE AND 4-METHOXYBENZOIC ACID FROM SINGLE SOLUTE AND AN ETHYL 4-AMINOBENZOATE:4-METHOXYBENZOIC ACID (1:1) BINARY SOLUTE SOLUTION AT pH 3.44 (0.5M IONIC STRENGTH)

Table 3.17 Date for the Sorption of ethyl 4-aminobenzoate on to Nylon 6 Powder from Single Solute and ethyl 4-aminobenzoate : 4-methoxybenzoic acid (1:1) Binary Mixed Solution pH 3.44 (ionic strength 0.5M) and the Temperature Range 5^{o} - 60^{o}. Concentration Range 0 - 10^{-3}M for Both Solutes.

Temperature ^{o}C	pH	Solute System	K $1Kg^{-1}$	Standard Deviation of K	t Statistic*	Intercept mol $Kg^{-1} x10^{4}$	Standard Deviation of Intercept x 10^{4}	Correlation Coefficient
5	3.42	Single Solute	26.3	0.5	-	4.11	1.78	0.999
15	3.42	Single Solute	24.6	0.6	0.14	8.69	2.41	0.997
		Binary Solute	24.5	0.4		5.49	1.72	0.999
20	3.44	Single Solute	24.8	0.4	0.00	7.50	1.80	0.999
		Binary Solute	24.8	0.4		2.67	1.28	0.999
30	3.44	Single Solute	22.3	0.6	0.26	4.24	2.76	0.998
		Binary Solute	22.1	0.5		3.02	1.91	0.998
40	3.44	Single Solute	21.4	0.3	0.00	5.36	1.36	0.999
		Binary Solute	21.4	0.6		3.32	2.71	0.997
50	3.45	Single Solute	18.6	0.3	0.63	5.18	1.32	0.991
		Binary Solute	18.8	0.1		1.66	0.61	0.998
60	3.46	Single Solute	16.6	0.6	0.74	1.67	2.75	0.999
		Binary Solute	16.1	0.3		2.32	1.41	0.999

* The number of data points for each isotherm was 10 and the $t_{tabulated}$ (P=0.05) value is 2.12.

Table 3.18 Data for the Sorption of 4-methoxybenzoic acid on to Nylon 6 Powder from Single Solute and ethyl 4-aminobenzoate : 4-methoxybenzoic acid (1:1) Binary Mixed Solution, pH 3.44 (ionic strength 0.5M) Over the Range 15^{o} - 60^{o} Concentration Range 0 - 1 x 10^{-3}M for Both Solutes.

Temperature ^{o}C	pH	Solute System	K $1Kg^{-1}$	Standard Deviation of K	t Statistic*	Intercept mol $Kg^{-1}x10^{4}$	Standard Deviation of Intercept x 10^{4}	Correlation Coefficient
15	3.42	Single Solute	36.4	0.4	0.94	3.77	1.30	0.999
		Binary Solution	37.0	0.5		-1.29	1.80	0.999
20	3.44	Single Solute	32.3	0.5	0.12	13.60	1.84	0.999
		Binary Solute	32.4	0.7		9.25	2.56	0.999
30	3.44	Single Solute	28.1	0.8	0.80	3.47	3.38	0.997
		Binary Solute	28.9	0.6		3.25	2.38	0.997
40	3.44	Single Solute	24.2	0.2	0.36	3.85	7.84	0.998
		Binary Solute	24.5	0.8		-3.91	3.45	0.996
50	3.45	Single Solute	19.9	0.4	1.24	2.88	1.88	0.998
		Binary Solute	19.2	0.4		3.62	2.07	0.998
60	3.46	Single Solute	15.2	0.2	0.63	2.21	0.88	0.999
		Binary Solute	15.6	0.6		8.47	0.28	0.999

* The number of data points for each Isotherm was 10 with the $t_{tabulated}$ (p=0.05) value is 2.12

Table 3.19 Thermodynamic Parameters for the Sorption of Ethyl 4-aminobenzoate and 4-methoxybenzoic acid by Nylon 6 Powder from Single and Binary Solute Solution at pH 3.44 (0.5M ionic strength).

Parameter	Temperature range ^{o}C	ethyl 4-aminobenzoate		4-methoxybenzoic acid	
		Single Solute	Binary Solute	Single Solute	Binary Solute
ΔH^{o} KJ mol^{-1}	5^{o} - 40^{o}	- 4.4 ± 0.6	- 4.6 ± 0.5	- 11.9 ± 0.7	- 11.66 ± 0.5
ΔH^{o} KJ mol^{-1}	40^{o} - 60^{o}	-11.0 ± 0.5	-12.1 ± 0.6	- 20.1 ± 2.2	- 19.16 ± 1.0
ΔG^{o} 293 KJ mol^{-1}	5^{o} - 40^{o}	- 7.8 ± 0.7	- 7.8 ± 0.7	- 8.5 ± 0.6	- 8.5 ± 0.1
ΔG^{o} 323 KJ mol^{-1}	40^{o} - 60^{o}	- 7.9 ± 0.2	- 7.7 ± 0.1	- 8.0 ± 0.1	- 7.9 ± 0.1
ΔS^{o} 293 J $deg^{-1}mol^{-1}$	5^{o} - 40^{o}	-11.7 ± 1.9	-10.9 ± 0.9	- 11.7 ± 0.3	- 10.8 ± 0.6
ΔS^{o} 323 J $deg^{-1}mol^{-1}$	40^{o} - 60^{o}	- 9.8 ± 0.8	-10.2 ± 0.7	- 37.4 ± 6.5	- 34.9 ± 1.1

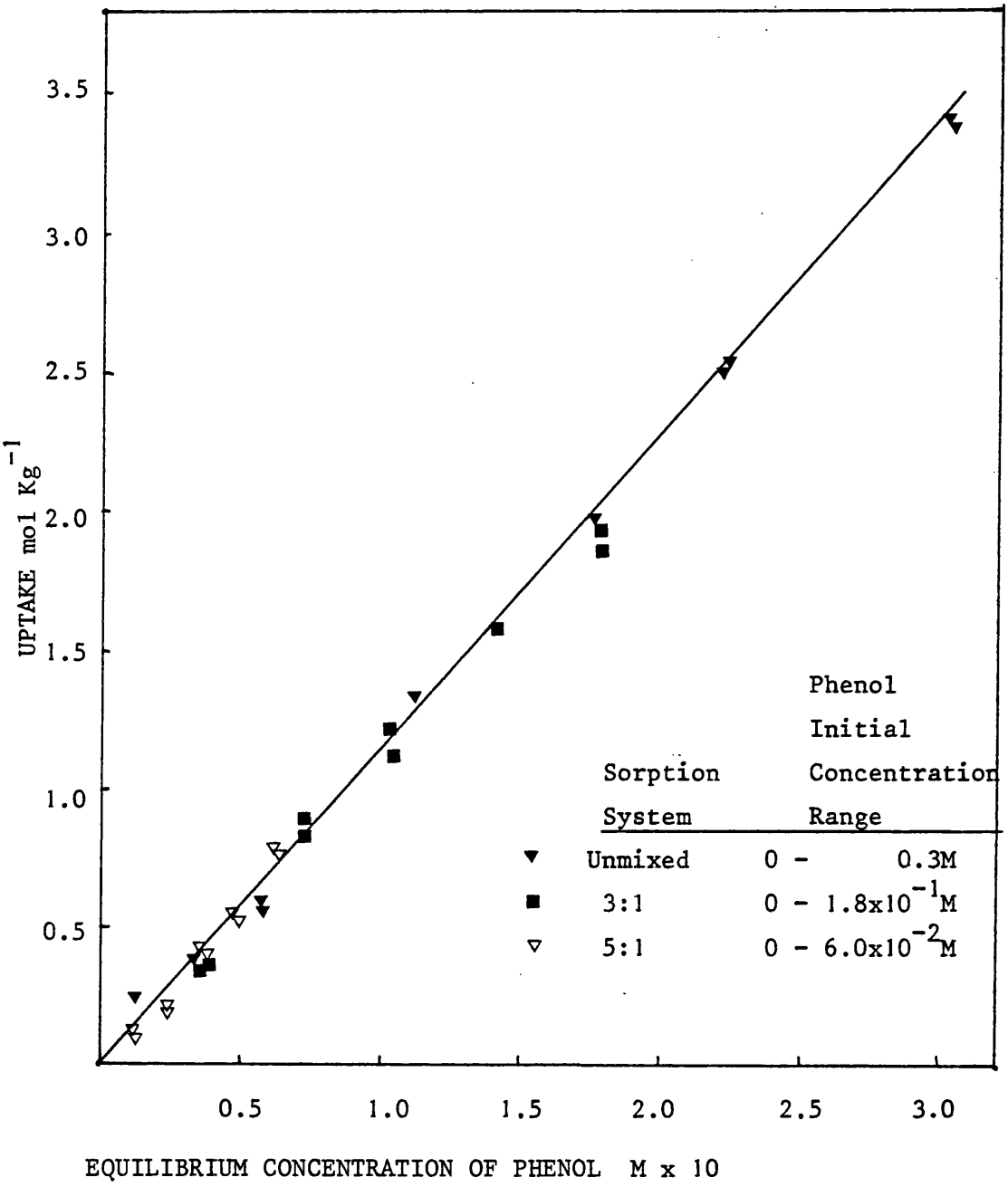


FIG 3.14 SORPTION ISOTHERMS FOR PHENOL BY NYLON 6 POWDER FROM SINGLE SOLUTE AND A PHENOL:4-NITROPHENOL (1:1) AND (3:1) BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGE OF 4-NITROPHENOL 0 - 6 x 10^{-2}M

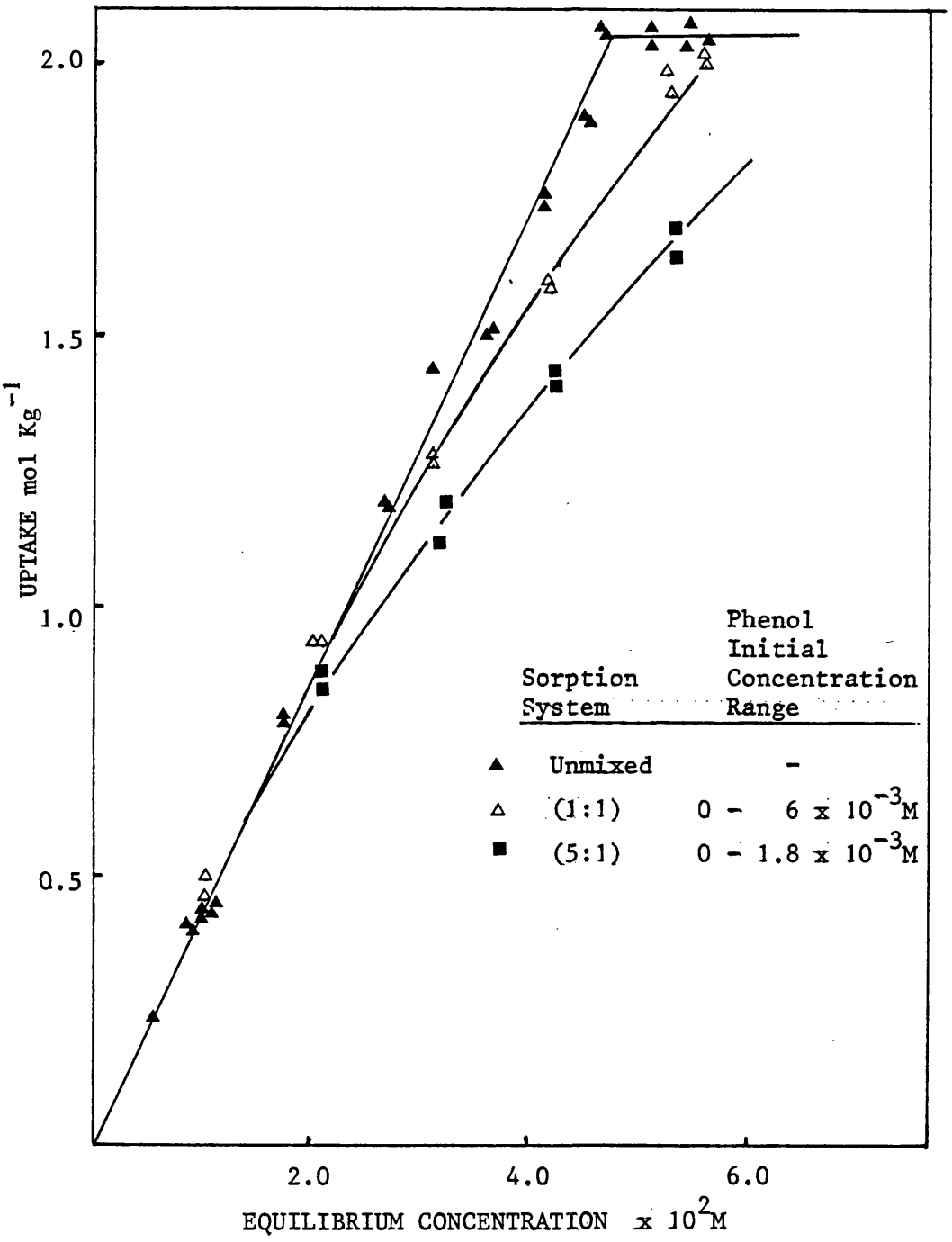


FIG 3.15 SORPTION ISOTHERMS FOR 4-NITROPHENOL ON TO NYLON 6 POWDER FROM SINGLE SOLUTE AND PHENOL: 4-NITROPHENOL (3:1) and (1:1) BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o}. 4-NITRO-PHENOL INITIAL CONCENTRATION 0 - 6 x 10^{-3}M

C_1 type and can be characterised by sorption K values which are summarised for each concentration range in table 3.20. The data from table 3.20 was submitted to an F-test to compare the K values for the three systems. The calculated value of the F statistic was less than the tabulated value indicating that no significant difference exists between the sorption characteristics of phenol binding from any of the four specified systems. The sorption of 4-nitrophenol is, however, affected by the presence of phenol as shown in figure 3.15. As the concentration of phenol present increases there is little evidence of competition in the initial region of the isotherm. At higher uptakes, however, the uptake of 4-nitrophenol is suppressed with respect to the single solute isotherm, the degree of suppression appearing to be a function of the concentration of phenol present in the system. Increasing the amount of phenol present to 5×10^{-3} M (5 times that of 4-nitrophenol) results in a further suppression in the uptake of 4-nitrophenol (figures 3.16a and 3.16b). The isotherm for phenol in this system in linear and superimposable on its single solute isotherm up to an uptake value of approximately 2.5 mol Kg^{-1}. After this point, the sorption of phenol shows a large increase relative to its single solute isotherm giving rise to a Z type sorption isotherm (Giles and Tolia 1964). The sorption isotherm of 4-nitrophenol is lowered in the presence of the high phenol concentration, but, above an uptake value of 1.5M Kg^{-1} there is a rise in uptake where again the system shows Z type isotherm behaviour. As the sorption isotherms for phenol and 4-nitrophenol from binary solute solution do not show C_1 type behaviour, experimental data are included in tables 3.21, 3.22 and 3.23.

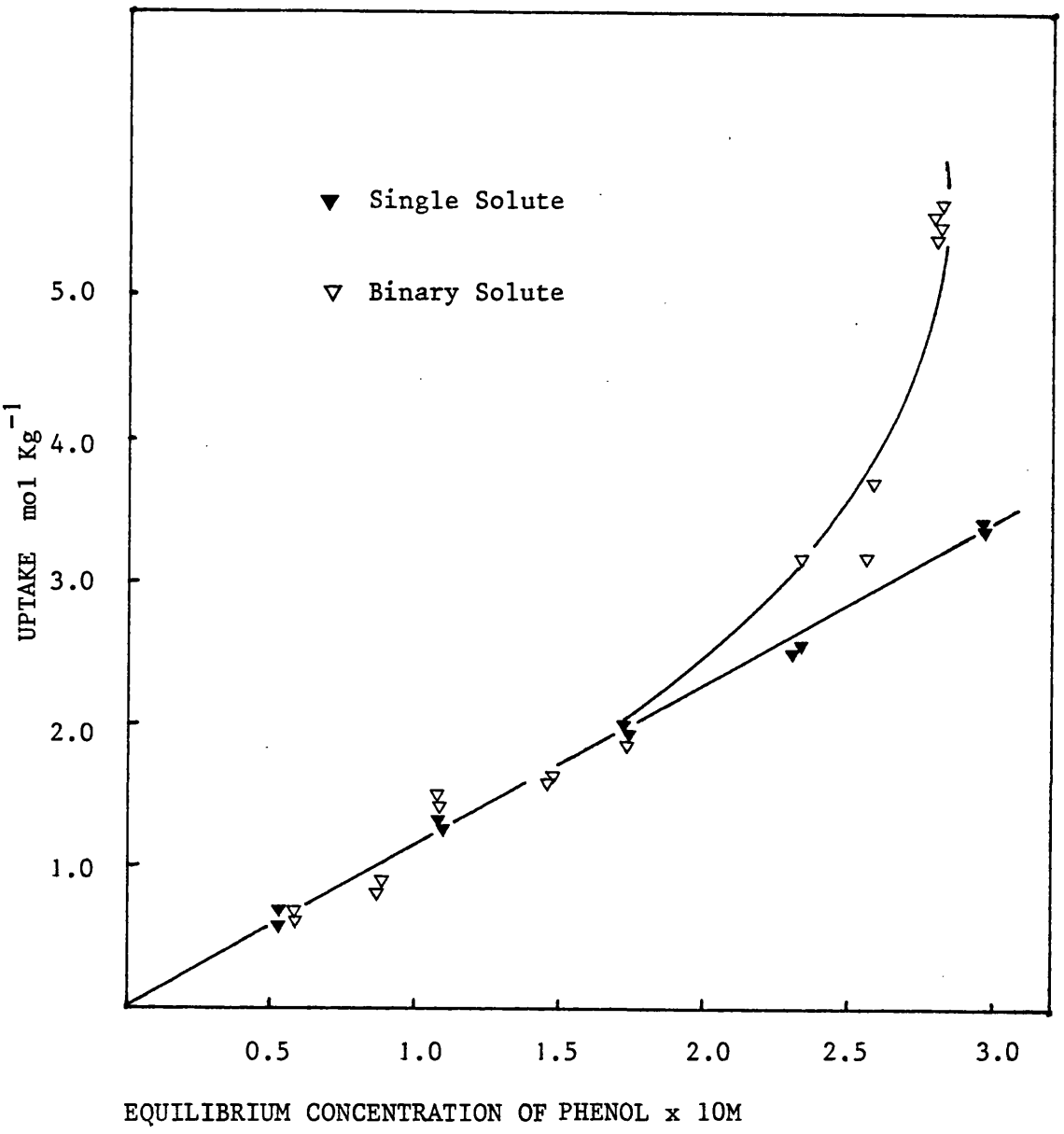


FIG 3.16a SORPTION ISOTHERMS FOR PHENOL BY NYLON 6 POWDER FROM SINGLE SOLUTE AND A PHENOL:4-NITROPHENOL (5:1) BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGES: PHENOL 0 - 0.3M ; 4-NITROPHENOL 0 - 6 x 10^{-2}M

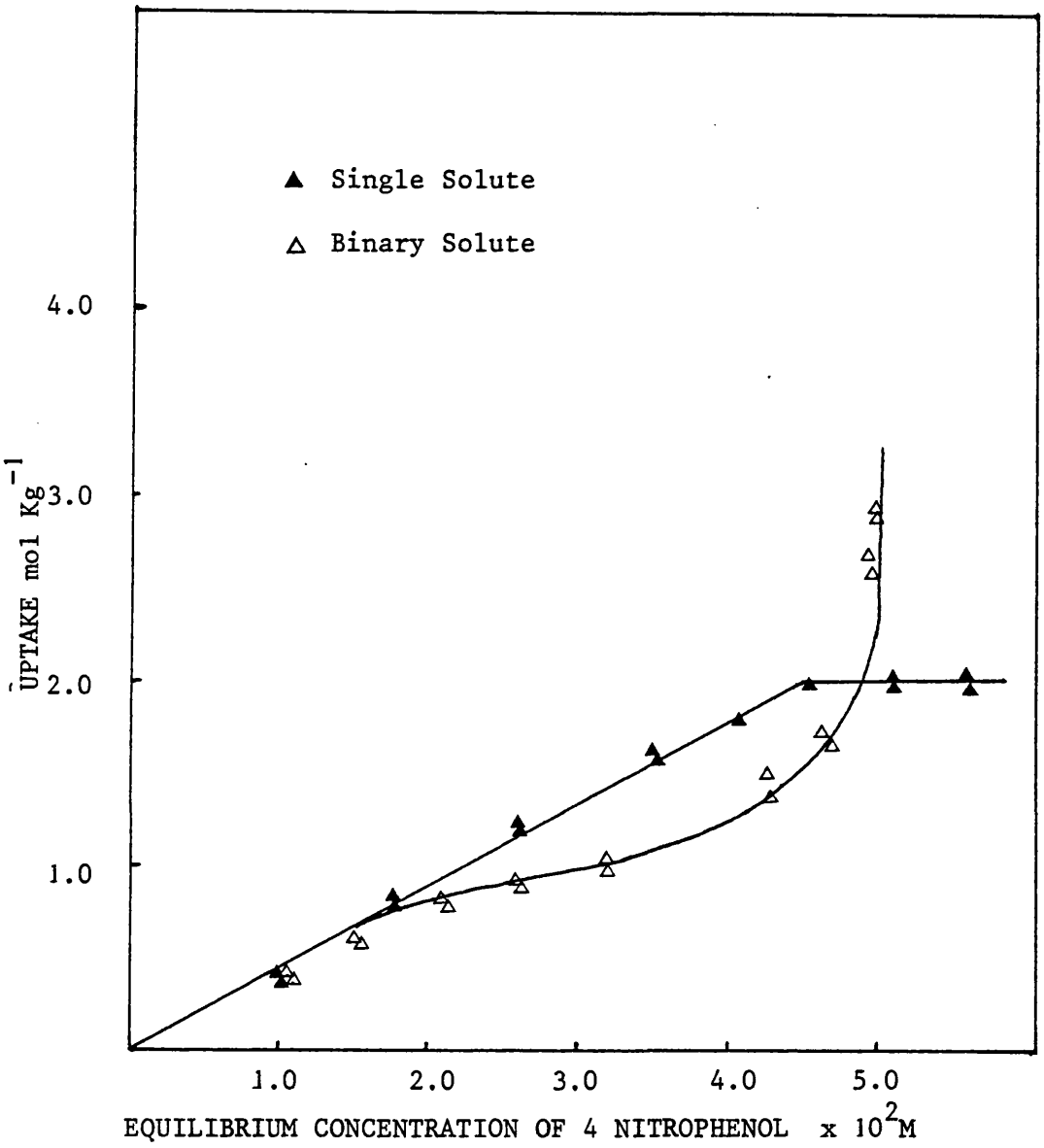


FIG 3.16b SORPTION ISOTHERMS FOR 4-NITROPHENOL BY NYLON 6 POWDER FROM SINGLE SOLUTE AND PHENOL:4-NITROPHENOL (5:1) BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AT 30°. CONCENTRATION RANGES: PHENOL, 0 - 0.3M, 4-NITROPHENOL, 0 - 6 x 10^{-2}M

Table 3.20 Isotherm Data for the Sorption of Phenol on to Nylon 6 over Different Concentration Ranges from Single and Binary Solute Solution pH 2.32 (0.5M Ionic Strength).

phenol : 4-nitrophenol	phenol concentration range	$K_{1kg^{-1}}$	Standard Deviation	Intercept mkg^{-1}	Standard Deviation	Correlation Coefficient
1 : 0	0 - 0.3M	11.7	0.3	-8.1×10^{-2}	6.1×10^{-2}	0.994
1 ; 0	0 - 0.01M	11.6	0.3	5.2×10^{-4}	5.7×10^{-4}	0.998
1 : 1	0 - 6×10^{-2}M	11.2	0.4	5.3×10^{-2}	4.9×10^{-2}	0.994
3 : 1	0.1.8x10^{-1}M	10.2	0.4	5.4×10^{-2}	5.1×10^{-2}	0.993

$F_{calc} = 0.06$ $F_{tabulated\ 3.31\ (P=0.05)} = 2.91$

Table 3.21 Data for the Sorption of phenol and 4-nitrophenol on to Nylon 6 Powder from a phenol : 4-nitrophenol (1:1) Binary Solute Solution pH 2.32 (ionic strength 0.5M) at 30^{o}.

Initial Concentration $Mx10^{2}$		Equilibrium Concentration $Mx10^{2}$		Sorbent weight(g)	Uptake mol Kg^{-1}	
phenol	4-nitrophenol	phenol	4-nitrophenol		phenol	4-nitrophenol
1.234	1.196	1.179	0.992	0.0403	0.137	0.51
1.234	1.196	1.179	0.013	0.0401	0.137	0.46
2.485	2.400	2.417	2.027	0.0395	0.172	0.94
2.485	2.400	2.417	2.027	0.0398	0.171	0.94
3.728	3.593	3.552	3.079	0.0400	0.440	1.28
3.708	3.593	3.552	3.079	0.0401	0.439	1.28
4.970	4.796	4.745	4.152	0.0402	0.560	1.60
4.970	4.796	4.745	4.152	0.0402	0.560	1.60
6.270	5.999	5.931	5.211	0.0397	0.843	1.99
6.270	5.999	5.931	5.211	0.0402	0.843	1.96

Table 3.22 Data for the Sorption of phenol and 4-nitrophenol on to Nylon 6 Powder from a phenol : 4-nitrophenol (3:1) Binary Solute Solution pH 2.32 (ionic strength 0.5M) at 30^{o}.

Initial Concentration		Equilibrium Concentration		Sorbent weight (g)	Uptake mol Kg^{-1}	
phenol x 10M	4-nitrophenol x 10^{2}M	phenol x 10M	4-nitrophenol x 10^{2}M		phenol	4-nitrophenol
0.369	1.204	0.354	1.013	0.0400	0.40	0.48
0.369	1.204	0.355	1.027	0.0398	0.36	0.45
0.735	2.379	0.701	2.027	0.0398	0.86	0.89
1.108	3.898	1.060	3.118	0.0400	1.20	1.20
1.108	3.598	1.063	3.147	0.0398	1.13	1.13
1.481	4.787	1.417	4.220	0.0401	1.59	1.41
1.481	4.787	1.416	4.360	0.0405	1.60	1.30
1.856	6.007	1.788	5.355	0.0398	1.70	1.63
1.856	6.007	1.782	5.330	0.0397	1.86	1.70

Table 3.23 Data for the Sorption of phenol and 4-nitrophenol on to nylon 6 Powder from a phenol : 4-nitrophenol (5:1) Binary Solute Solution pH 2.32 (ionic strength 0.5M) at 30^{o}.

Initial Concentration		Equilibrium Concentration		Sorbent weight (gramme)	Uptake mol Kg^{-1}	
phenol x 10M	4-nitrophenol x 10^{2}M	phenol x 10M	4-nitrophenol x10^{2}M		phenol	4-nitrophenol
0.604	1.188	0.576	1.017	0.0404	0.67	0.42
0.604	1.188	0.576	1.025	0.0399	0.68	0.41
0.900	1.786	0.871	1.544	0.0399	0.73	0.61
0.900	1.786	0.871	1.544	0.0405	0.72	0.60
1.216	2.403	1.154	2.068	0.0404	1.54	0.83
1.216	2.403	1.156	2.071	0.0405	1.48	0.82
1.500	2.976	1.437	2.603	0.0399	1.58	0.94
1.500	2.976	1.433	2.603	0.0402	1.57	0.93
1.819	3.576	1.738	3.158	0.0402	2.01	1.04
1.819	3.576	1.747	3.192	0.0402	1.79	0.96
Plasticisation						
2.472	4.863	2.347	4.287	0.0397	3.15	1.45
2.732	5.355	2.582	4.660	0.0402	3.73	1.73
2.732	5.355	2.606	4.686	0.0398	3.17	1.68
3.018	5.999	2.793	4.957	0.0398	5.66	2.59
3.022	6.007	2.798	4.838	0.0402	5.58	2.94
3.022	6.007	2.798	4.838	0.0402	5.58	2.92

Close agreement between values of uptake obtained from replicate determinations in the high uptake region of the Z isotherm (figure 3.21) was not observed. This is probably due to the structural instability of the polymer above the critical value of uptake where plasticization occurs.

3.2.5.2.1 The Effect of Temperature.

The isotherms of phenol and 4-nitrophenol were determined over the range 10^{o} - 50^{o} from single solute and a phenol : 4-nitrophenol (1:1) binary mixed solution. Isotherms were measured over a concentration range of 0 - $3x10^{-2}$ M to ensure that 4-nitrophenol remained within the C_1 linear region of the isotherm. The buffer solution was sensitive to temperature, changing from 2.30 to 2.35 over the range studied. This effect was not of significance as the pKa values of both solutes were more than 2 pH units away from the extremes of this pH range. Isotherm data was plotted as isochores, and used as a basis for calculating thermodynamic parameters associated with the overall sorption process. Data for the sorption of 4-nitrophenol and phenol at various temperatures are given in tables 3.24 and 3.25. Comparison of the K values for single and binary solute system isotherms indicates that there is no significant difference between them at any temperature at the 95% level of significance. The data in tables 3.24 and 3.25 is shown plotted in figure 3.17.

The isochores for the phenolic compounds do not show the inflexion which is characteristic of the benzoic acid derivative isochores. Thermodynamic parameters associated with the interaction of phenol and 4-nitrophenol from single and binary solute solution are given in table 3.26. Values for the phenolic derivatives are, however, given at two temperatures to enable comparison between the phenolic compounds and those for the benzoic acid derivatives (table 3.19).

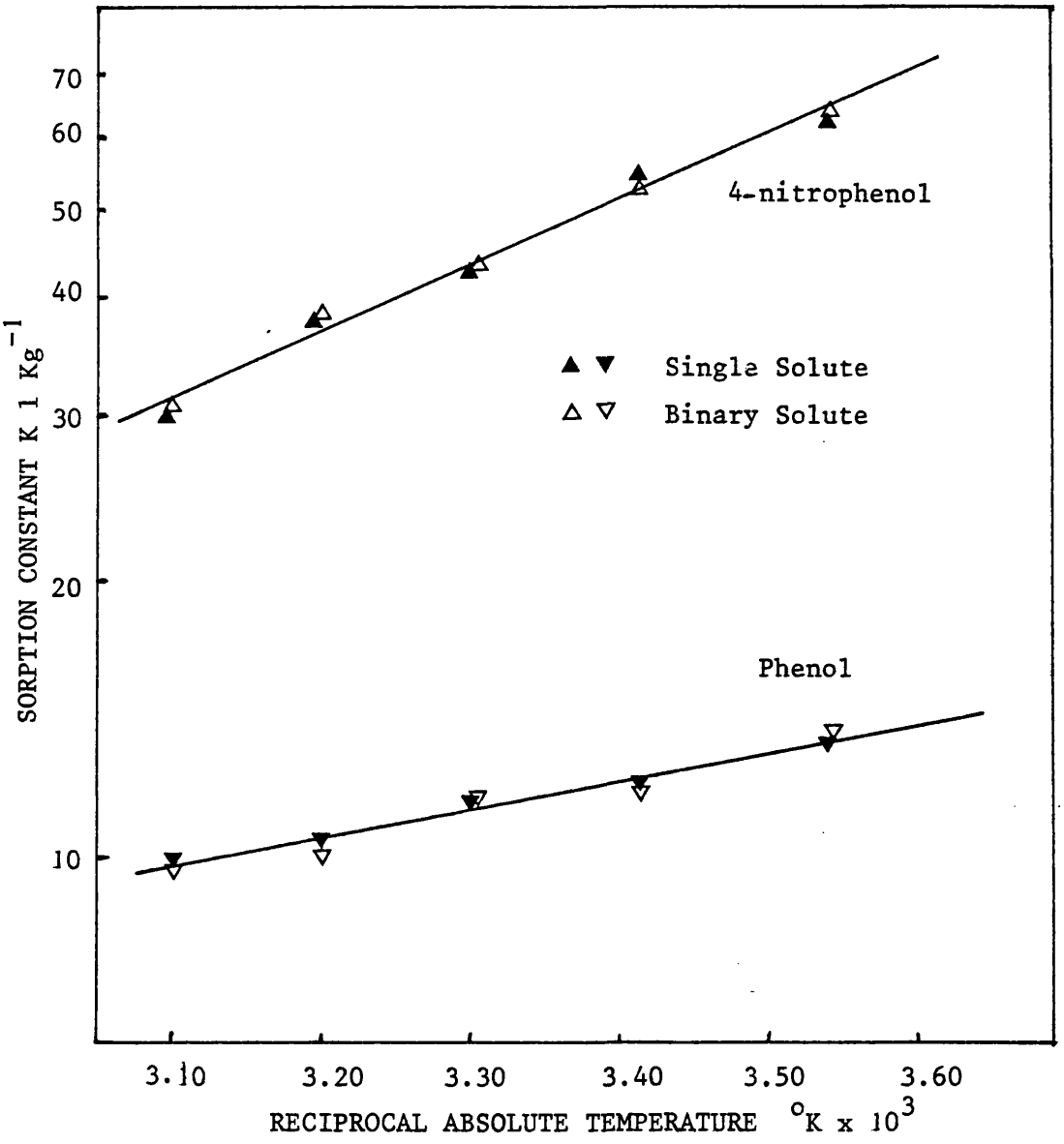


FIG 3.17 VAN'T HOFF ISOCHORES FOR THE EFFECT OF TEMPERATURE ON THE SORPTION OF PHENOL AND 4-NITROPHENOL FROM SINGLE SOLUTE AND A PHENOL:4-NITROPHENOL (1:1) BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH).

Table 3.24 Data for the Sorption of phenol from Single Solute and a phenol : 4-nitrophenol (1:1) Binary Mixed Solution at pH 2.32 (ionic strength 0.5M) over the range 10^{o} - 50^{o} Initial Concentration Range 0 - 3×10^{-2} M

Temperature ^{o}C	Solution System	K_{-1} 1Kg	Standard Deviation of K	t * statistic	Intercept mol Kg^{-1}	Standard Deviation of Intercept	Correlation Coefficient
10	single solute	13.6	0.2	0.95	0.83	0.39	0.998
	binary solute	14.2	0.6		-1.34	0.90	0.993
20	single solute	12.2	0.2	0.45	0.51	0.41	0.998
	binary solute	12.0	0.4		0.67	0.55	0.996
30	single solute	11.6	0.3	0.20	0.52	0.57	0.998
	binary solute	11.7	0.4		-0.48	1.72	0.996
40	single solute	10.5	0.1	0.98	-0.56	0.24	0.999
	binary solute	10.0	0.5		-1.50	0.87	0.990
50	single solute	10.1	0.2	0.79	1.49	3.09	0.996
	binary solute	9.6	0.6		0.33	0.83	0.986

* All sorption isotherms were composed of 10 data points. The $t_{tabulated}$ (P=0.05) value is 2.12.

Table 3.25 Data for the Sorption of 4-nitrophenol from Single Solute and a phenol : 4-nitrophenol (1:1) Binary Mixed Solution, pH 2.32 Ionic Strength 0.5M over the Range 10^{o} - 50^{o}. Initial Concentration Range $0\text{-}3\times10^{-2}$M.

Temperature ^{o}C	Solution	K $1Kg^{-1}$	Standard Deviation	t* statistic	Intercept MKg^{-1}	Standard Deviation of Intercept	Correlation Coefficient
10	single solute	63.1	1.1	0.18	-1.60	1.28	0.999
	binary solution	63.4	1.3		-1.84	1.16	0.998
20	single solute	55.7	0.6	1.39	-1.58	0.73	0.999
	binary solution	54.7	0.4		-0.73	0.41	0.998
30	single solute	42.3	0.9	0.00	-0.04	0.26	0.998
	binary solution	42.3	0.4		±0.00	0.14	0.998
40	single solute	38.6	0.4	0.94	-0.06	0.56	0.999
	binary solution	39.2	0.5		-0.09	0.50	0.999
50	single solute	29.9	0.5	0.26	-1.04	0.67	0.999
	binary solution	30.1	0.6		-0.55	0.78	0.998

* All isotherms consisted of 10 data points. The $t_{tabulated}$ (P=0.05) value is 2.12.

Table 3.26 Thermodynamic Parameters for the Sorption of phenol and 4-nitrophenol by Nylon 6 Powder from Single Solute Solution at pH 2.32 (ionic strength 0.5M).

Parameter	phenol		4-nitrophenol	
	Single Solute	Binary Solute	Single Solute	Binary Solute
ΔH^{o} KJ mol^{-1}	-5.7 ± 0.4	-7.4 ± 0.5	-14.1 ± 1.3	-13.8 ± 0.9
ΔH^{o} KJ mol^{-1}	-5.7 ± 0.4	-7.4 ± 0.5	-14.1 ± 1.3	-13.8 ± 0.9
ΔG^{o}_{293} KJ mol^{-1}	-6.1 ± 0.04	-6.1 ± 0.04	-9.8 ± 0.03	-9.7 ± 0.05
ΔG^{o}_{323} KJ mol^{-1}	-6.3 ± 0.03	-6.1 ± 0.08	-9.8 ± 0.1	-9.1 ± 0.15
ΔS^{o}_{293} J $deg^{-1}mol^{-1}$	-1.40 ± 2.3	-4.4 ± 3.10	-14.7 ± 4.3	-16.0 ± 5.20
ΔS^{o}_{323} J $deg^{-1}mol^{-1}$	-2.0 ± 1.2	-1.2 ± 2.6	-13.3 ± 3.7	-14.6 ± 4.72

3.2.5.3. Uptake from Binary Solutes of Phenolic and Benzoic Acid Derivatives by Nylon 6 Powder.

Isotherms for the sorption of solutes from 4-nitrophenol : 4 methoxybenzoic acid (5:1) and 4-nitrophenol : ethyl 4-aminobenzoate (1:1) binary solute solutions were determined. The 4-nitrophenol : 4-methoxybenzoic acid (5:1) solutions were formulated with concentrations of 4-nitrophenol and 4-methoxybenzoic acid over the range $0-5x10^{-3}$M and $0-1x10^{-3}$M respectively.

The 4-nitrophenol : ethyl 4-aminobenzoate (5:1) systems were formulated with concentrations of both 4-nitrophenol and ethyl 4 - aminobenzoate over the range $0-5x10^{-3}$M. Isotherm data is given in table 3.27.

Comparison of the single and binary solute K values by t test showed them to be not significantly different at the 95% level of significance.

3.3 THE SORPTION OF MODEL SOLUTES BY UNCOATED AND NYLON 6 COATED ACTIVE CARBON.

3.3.1 General Method for the Determination of Sorption.

The apparatus used for the experimental determination of solute uptake by nylon 6 powder has been described in Section 3.2.1. The standard procedure for isothermal equilibrium and sampling was also applied to the carbon systems. Sorption experiments were carried out at pH2.32 (ionic strength 0.5M) maintained by McIlvaine's citrate phosphate buffer at 30^{o}. Preliminary studies showed that the model solutes were completely removed from solution using 200mg of sorbent granules suspended in 10ml of solution. It was necessary, therefore, to reduce the granule weight to 20mg and suspend the granules in 50ml

Table 3.27 Isotherm Data for the Sorption of Solutes from 4-nitrophenol : 4-methoxybenzoic acid (5:1) and 4 nitrophenol : ethyl 4-aminobenzoate (1:1) Binary Solute Solutions at pH 2.32 (0.5M ionic strength) and 30° on to nylon 6 powder

Solute	K value lKg^{-1}	Standard Deviation of K	t statistic[4****]	Intercept $mol\ Kg^{-1} \times 10^4$	Standard Deviation of Intercept $\times 10^4$	Correlation Coefficient
4-nitrophenol	42.3*	0.9		3.83	2.57	0.998
	41.2**	0.3	1.16	10.10	4.95	0.999
	43.1***	0.5	0.78	0.87	5.51	0.999
ethyl 4-amino-benzoate	9.3*	0.2		4.27	0.66	0.999
	9.8***	0.3	1.39	6.83	5.10	0.996
4-methoxybenzoic acid	29.2*	0.3		7.16	1.35	0.999
	29.7**	0.3	1.18	0.95	1.10	0.999

K values
* - Single solute system
** - 4-nitrophenol : 4-methoxybenzoic acid (5:1) system
*** - 4-nitrophenol : ethyl 4-aminobenzoate (1:1) system
**** - All isotherms consisted of 10 data points $t_{0.05} = 2.12$

of solution. The smaller sorbent weight of 20mg was measured using a high precision balance which could read accurately to five decimal places i.e. to 10^{-5} gramme. In all cases a measurable change in solution concentration occurred during contact with the sorbent while the equilibrium concentration was well within the sensitivity limits of the spectrophotometric assay.

3.3.2 Determination of the Equilibration Time.

The procedure for the determination of the equilibration time was the same as that described in Section 3.2.2. The variability of the uptake data was found to be much higher compared to those obtained for the nylon 6 powder equilibration time determination. The data for the equilibration time of 4-nitrophenol was used to determine the sources of error. Table 3.28 gives the experimental data for the determination of the 4-nitrophenol equilibration time.

The data in Table 3.28, typical of equilibration time data for the model solutes, shows that the coefficient of variation for the uptake is 7.05%. This would appear to arise from the 2.56% and 2.16% coefficients of variation for the equilibrium concentration and sorbent weight data respectively. Due to the granular nature of the carbon adsorbent, it is not possible to reproduce the exact weight in the replicate flasks, which will account for the variability of the equilibrium concentration values for the given value of initial concentration. If the activity of the sorbent is high, as is the case here, small changes in equilibrium concentration can give rise to wide variation in uptake. As the plot of uptake versus time (figure 3.19) does not take into account the effect of the inter-relationship between uptake and equilibrium concentration it will be subject to error.

An alternative method of representing the extent of solute uptake

Table 3.28 Data for the Sorption of 4-nitrophenol on to Active Carbon at pH 2.32 (0.5M ionic strength) and 30^{o} over a Time Period of Fourteen Days.

Time Days	Initial Concentration $\times 10^{3}$ M	Equilibrium Concentration $\times 10^{3}$ M	Sorbent Weight (gramme)	Uptake mol Kg^{-1}	Percentage Residual Concentration
3	5.061	3.561	0.0201	3.73	70.3
		3.420	0.0199	4.12	67.5
5		3.502	0.0200	3.90	69.1
		3.641	0.0210	3.38	72.0
7		3.662	0.0198	3.54	72.4
		3.531	0.0201	3.81	69.7
9		3.596	0.0211	3.48	71.0
		3.598	0.0200	3.68	71.0
11		3.544	0.0199	3.80	69.9
		3.472	0.0198	4.02	68.5
13		3.327	0.0202	4.31	65.7
		3.525	0.0205	3.76	69.5
Coefficient of Variation		2.56%	2.16%	7.05%	2.58%

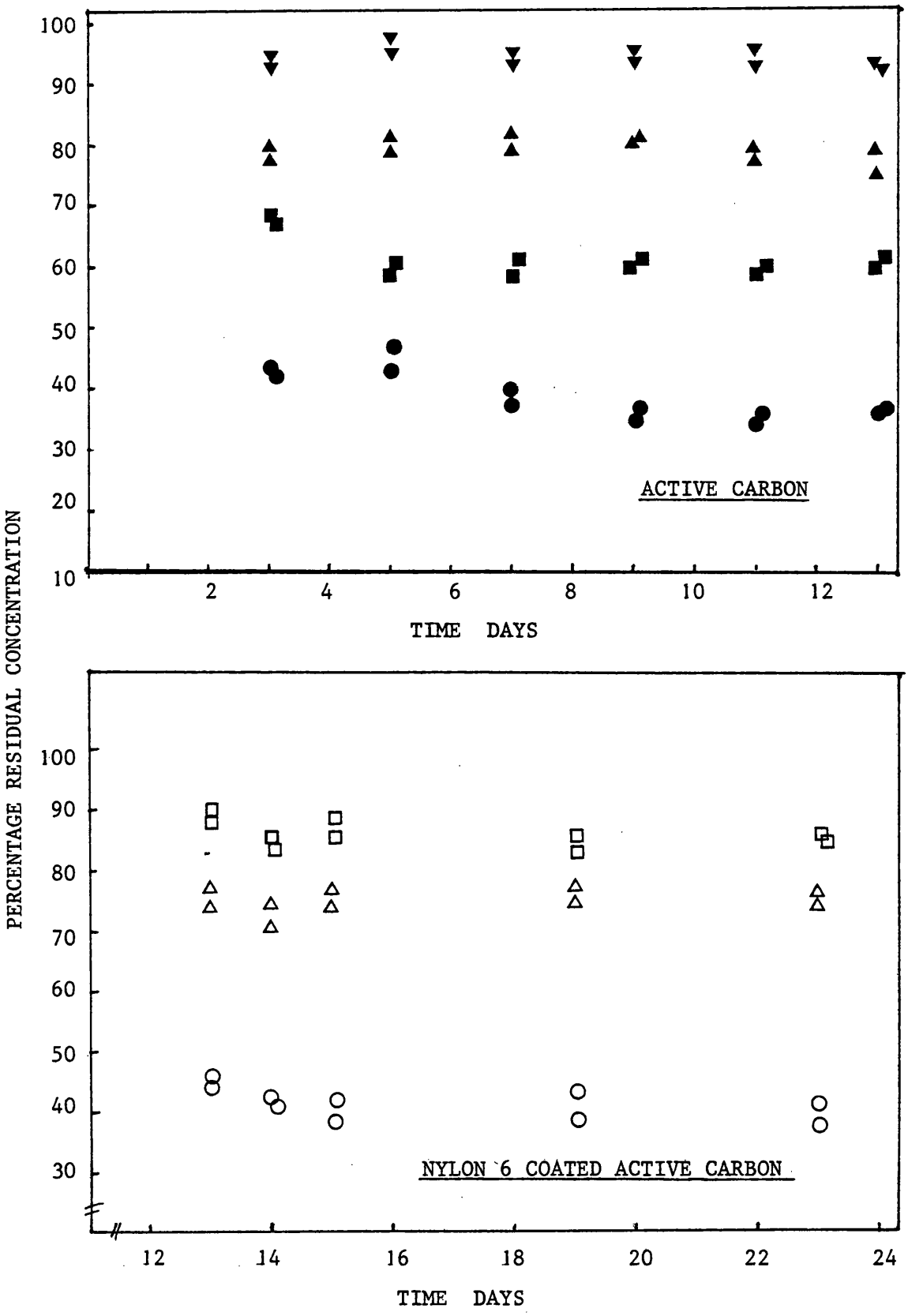


FIG 3.19 EQUILIBRATION TIME DATA FOR THE ADSORPTION OF THE MODEL SOLUTES BY UNCOATED AND NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH).

Ethyl 4-aminobenzoate ●○ 4-nitrophenol ▲ △

4-methoxybenzoic acid ■□ phenol ▽

would be to use the percentage residual concentration. The percentage residual concentration is related to uptake provided that variation in solution volume and sorbent weight in the system is small. The percentage residual concentration appears to be less sensitive to variability in sorbent weight with a coefficient of variation of 2.58% as opposed to 7.05% for uptake. It was, therefore, considered preferable to assess the extent of attainment of equilibrium using plots of percentage residual concentration instead of uptake versus time.

The equilibrium time data for all four model solutes on active carbon and nylon 6 coated active carbon are given in Table 3.29 and shown plotted in figure 3.19. The ultra violet absorption spectra of the four model solutes did not show any change whilst in contact with active carbon granules. The spectrum of phenol did however show signs of change after 23 days in contact with nylon 6 coated active carbon suggesting that this solute was undergoing some form of chemical change (figure 3.20). Phenol was not, therefore, included in sorption studies involving the nylon 6 coated active carbon. The data in figure 3.19 suggests that shaking times of 10 and 21 days for sorption on to active carbon and nylon 6 coated active carbon respectively are sufficient to ensure that equilibrium is fully established.

3.3.3 The Sorption of the Model Solutes from Single Solute Solution.

The non-linear nature of the isotherms obtained for sorption of the model solutes by active carbon required a greater number of data points to characterise the uptake profile than that for nylon 6. Consquently, eight concentrations of each solute were used; replicates were performed as before. Due to the variation of sorbent weight, the two uptake-

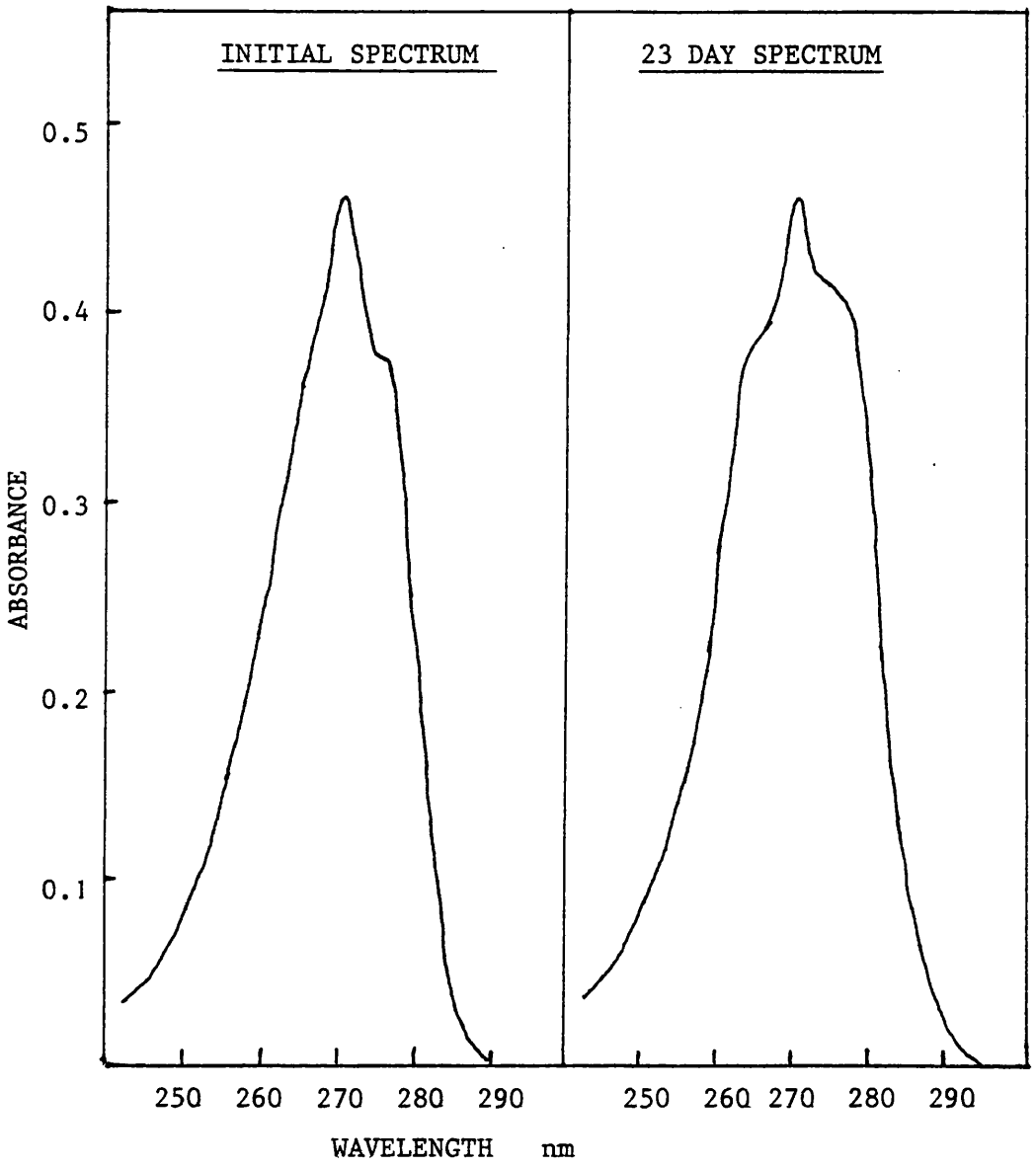


FIG 3.20 THE ULTRAVIOLET ABSORPTION SPECTRUM OF PHENOL BEFORE AND AFTER CONTACT WITH NYLON 6 COATED ACTIVE CARBON FOR A PERIOD OF 23 DAYS AT pH 2.32 (0.5M IONIC STRENGTH)

Table 3.29 Equilibrium Time Data for the Sorption of the Model Adsorbates by Uncoated and Nylon 6 Coated Active Carbon at pH 2.32 (0.5 ionic strength) and 30°.

ACTIVE CARBON

Time Days	Percentage Residual Concentration in the Liquid Phase			
	4-nitrophenol	phenol	4-methoxybenzoic acid	ethyl 4-aminobenzoate
3	70.3	85.1	33.1	58.8
	67.5	83.9	33.9	58.4
5	69.1	85.1	33.0	49.9
	72.0	87.8	36.9	50.4
7	72.4	84.0	24.1	49.3
	69.7	85.5	29.8	51.9
9	71.0	86.2	24.2	50.2
	71.0	84.7	25.1	50.4
11	69.9	85.3	24.9	49.3
	68.5	83.1	25.8	49.4
13	65.7	84.5	25.9	50.0
	69.5	84.4	25.8	50.3
nominal granule weight (g)	0.02	0.02	0.02	0.02
solution volume (ml)	50	50	50	50
Initial Concentration (M)	5.06×10^{-3}	5.00×10^{-3}	1.30×10^{-3}	5.50×10^{-3}

Table 3.29 - Continued ...

NYLON 6 COATED ACTIVE CARBON

Time Days	Percentage Residual Concentration in the Liquid Phase			
	4-nitrophenol		4-methoxybenzoic acid	ethyl 4-aminobenzoate
13	73.9		44.6	89.0
	77.2		41.0	90.2
14	71.5		42.0	84.1
	74.7		46.7	85.0
15	77.2		38.2	89.9
	74.4		41.7	85.6
19	74.7		43.0	83.0
	77.9		38.2	85.4
23	74.5		37.0	86.4
	76.1		40.8	86.0
nominal granule weight(g)	0.02		0.02	0.02
solution volume (ml)	50		50	50
Initial Concentration(M)	5.01×10^{-3}		1.01×10^{-3}	1.01×10^{-3}

equilibrium concentration data points obtained from a given initial solute concentration would not be identical but would be expected to fall on the isotherm at a similar location. If one of the pair of data points appeared anomalous as assessed by visual inspection of the isotherm the supernatant was reassayed. If the data point still did not fall on the isotherm its determination was repeated.

Initially, the sorption isotherm of 4-nitrophenol on to uncoated active carbon was determined to assess the reproducibility of the standard procedure. Data for the adsorption isotherm over an initial concentration range 0 - $5x10^{-3}$ M is given in Table 3.30 and is shown plotted in figure 3.21. The isotherms were of the L_1 type and visual inspection shows the replicate isotherms to be superimposable.

For comparative purposes the sorption isotherms for all four model solutes are presented in two ways. Firstly, the sorption isotherms for the model solutes on uncoated active carbon are shown in figure 3.22. The open symbols on the model solutes indicate the position of uptake values obtained by the adsorb : desorb method described in Section 3.2.4.1. The alignment of both the high and low equilibrium uptakes corresponding to the adsorption and desorption equilibrium confirm that the interaction is reversible. The data in figure 3.22 shows that the observed rank order of affinity for the uncoated active carbon is:-

4 methoxybenzoic acid > 4-nitrophenol > ethyl 4-aminobenzoate >phenol

Secondly the isotherms of 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate on both uncoated and nylon 6 coated active carbon are shown in figures 3.23 to 3.25, respectively. As 4-nitrophenol has a higher solubility than either of the other two solutes, the concentration range of the isotherm determination was extended

Table 3.30 Data for the Sorption of 4-nitrophenol by Active Carbon at pH2.32 (ionic strength 0.5M) and 30° Initial Concentration Range 0 - 5×10^{-3} M.

Initial Concentration $\times 10^{3}$ M	Equilibrium Concentration $\times 10^{3}$ M	Sorbent Weight gramme	Uptake M Kg^{-1}
DETERMINATION I			
0.133	0.050	0.0217	0.19
0.260	0.095	0.0204	0.40
0.522	0.153	0.0211	0.88
0.776	0.415	0.0181	0.99
0.991	0.446	0.0204	1.33
1.041	0.442	0.0182	1.65
2.006	1.068	0.0217	2.16
3.023	1.847	0.0195	3.01
3.961	2.503	0.0217	3.36
3.967	2.478	0.0231	3.22
4.965	3.381	0.0217	3.65
5.074	3.466	0.0219	3.67

Table 3.30 - Continued ....

Initial Concentration $\times 10^{3}$ M	Equilibrium Concentration $\times 10^{3}$ M	Sorbent Weight gramme	Uptake $M\ Kg^{-1}$
DETERMINATION II			
0.133	0.050	0.0216	0.30
0.260	0.096	0.0199	0.45
0.522	0.153	0.0196	1.07
0.627	0.271	0.0202	0.88
0.627	0.248	0.0207	0.92
0.776	0.212	0.0205	1.38
1.256	0.636	0.0200	1.59
1.256	0.575	0.0201	1.69
1.884	0.929	0.0224	2.13
1.884	0.938	0.0233	2.03
2.534	1.312	0.0240	2.60
2.534	1.363	0.0204	2.87
3.170	1.888	0.0230	2.79
3.792	2.379	0.0197	3.58

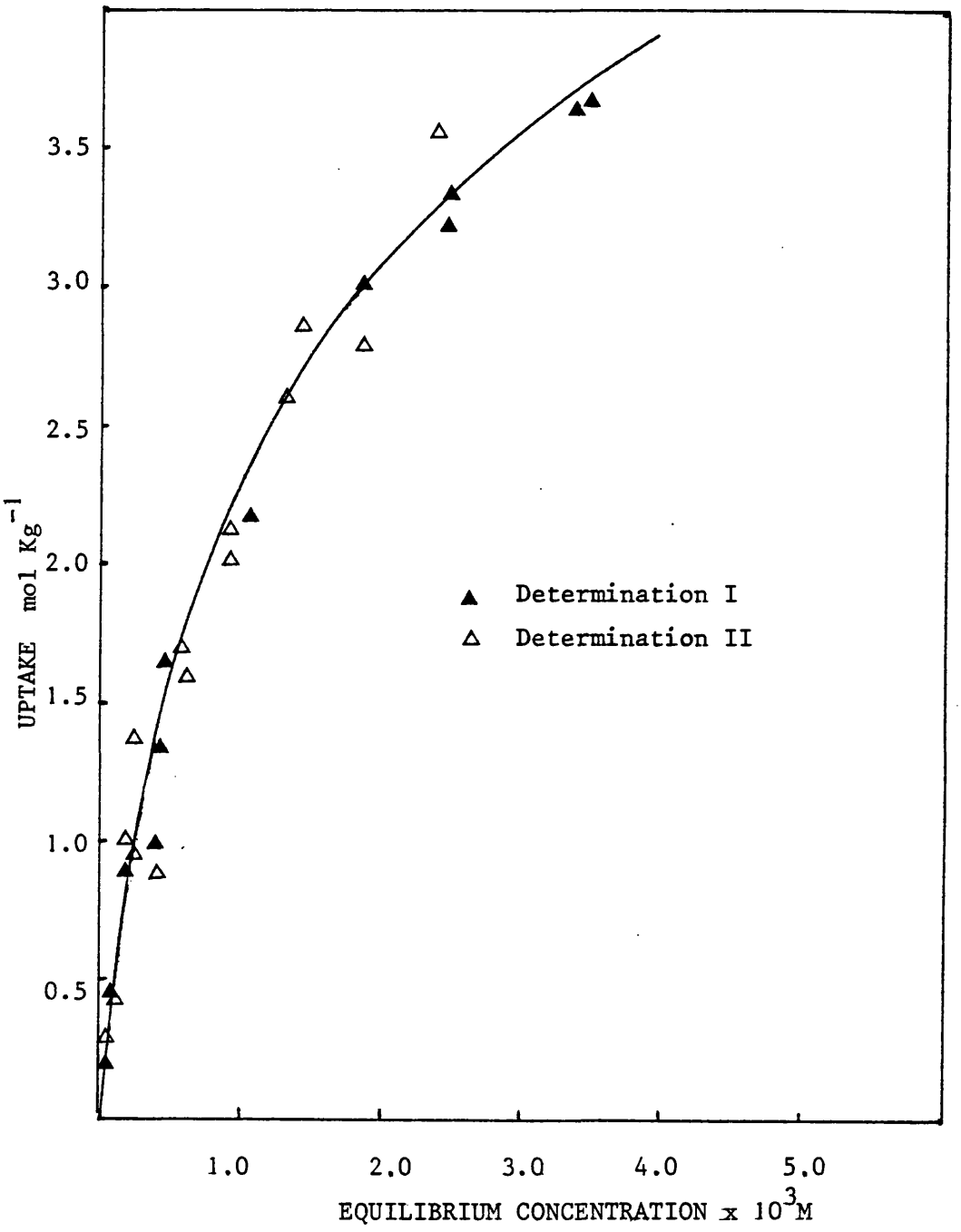


FIG 3.21 REPLICATE SORPTION ISOTHERMS OF 4-NITROPHENOL BY ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGE 0 - 5 x 10^3M

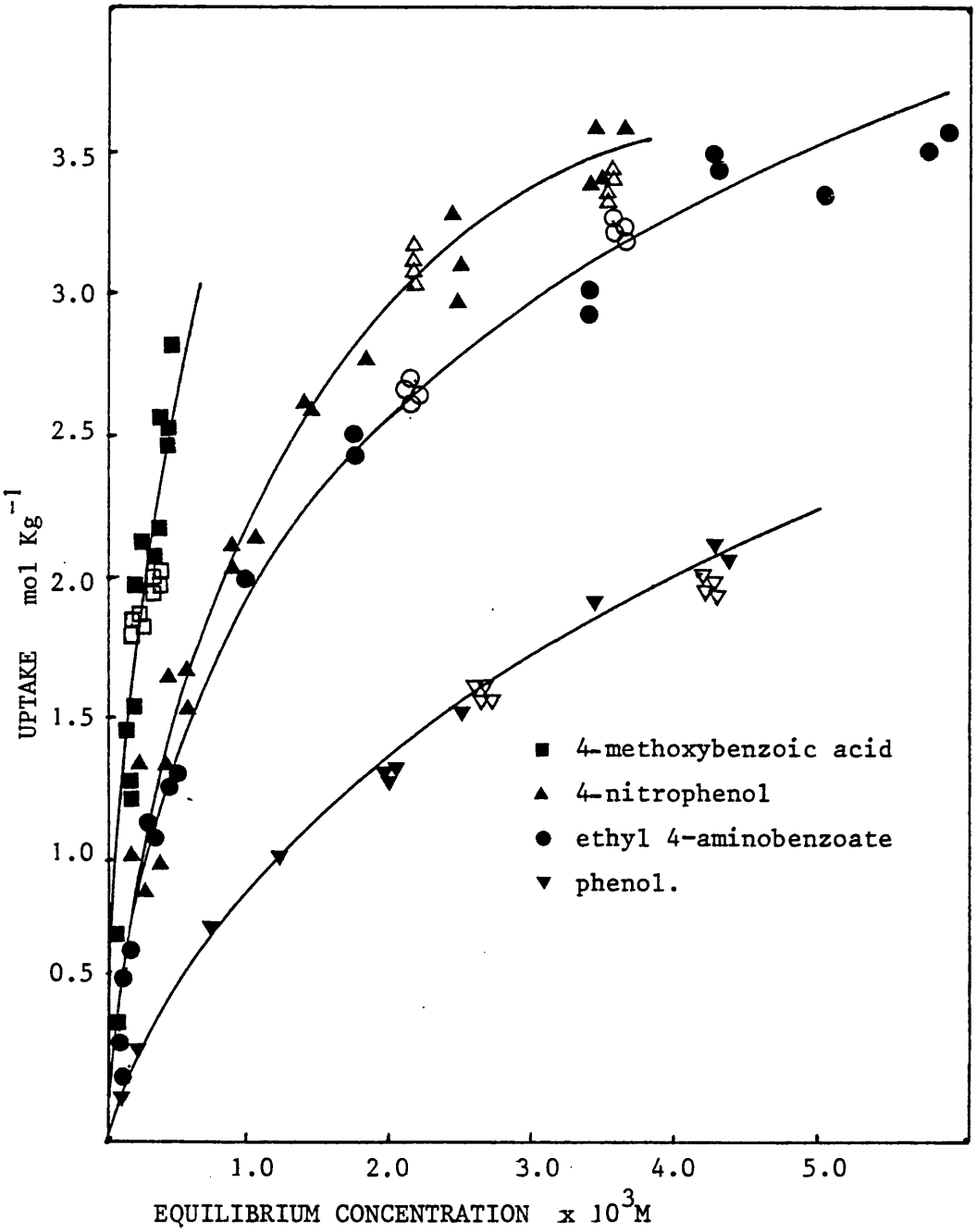


FIG 3.22 SORPTION ISOTHERMS FOR THE INTERACTION OF THE FOUR MODEL SOLUTES WITH UNCOATED AND NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AT 30°. INITIAL CONCENTRATION RANGES: 4 - METHOXYBENZOIC ACID 0 - 1.5 x 10^{-3}M, ALL OTHERS 0 - 5 x 10^{-3}M

Closed Symbols - Adsorption data Open Symbols - Adsorb/desorb data

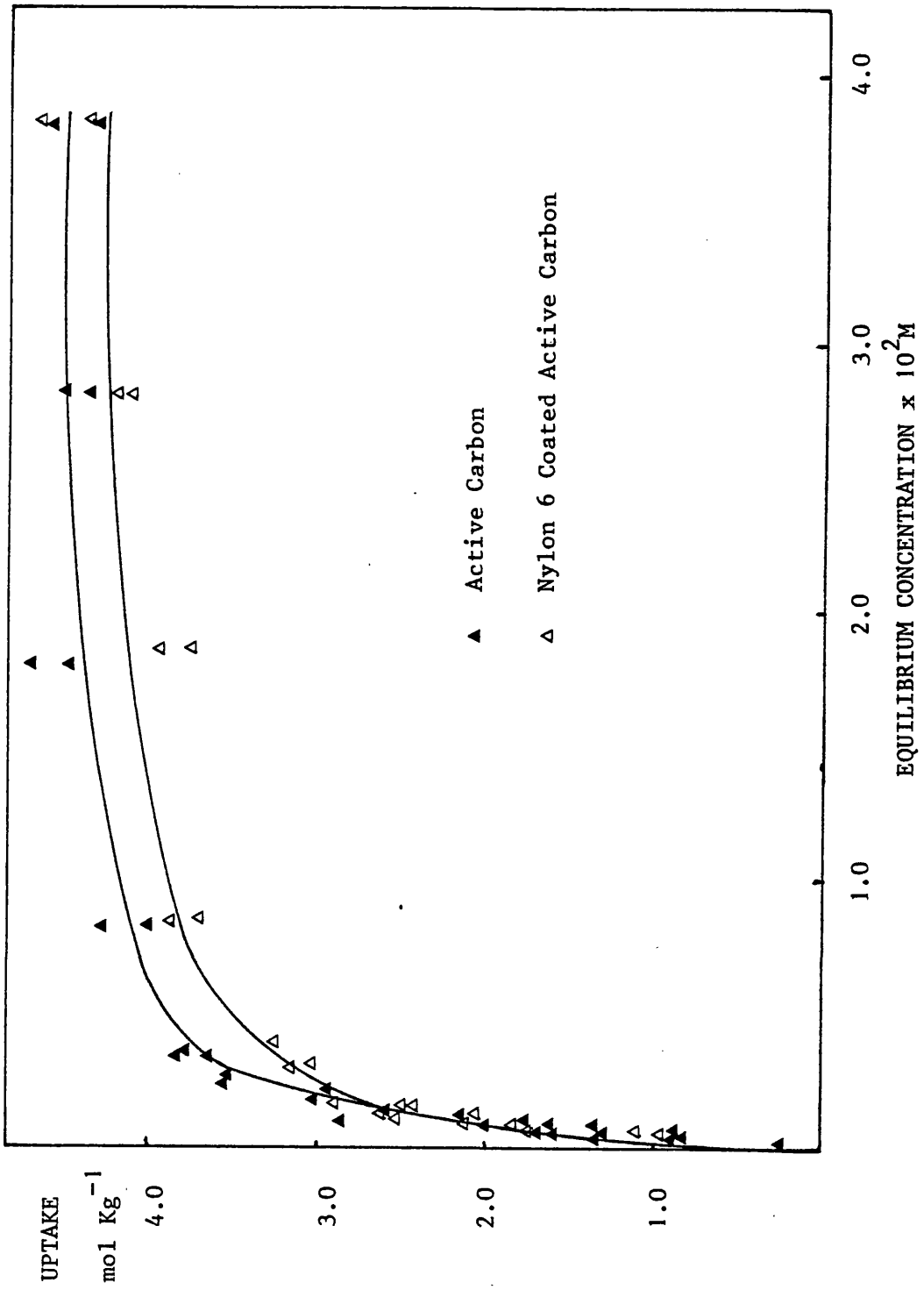


FIG 3.23 SORPTION ISOTHERMS OF 4-NITROPHENOL ON TO UNCOATED AND NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION 0 - 5 x 10^{-2}M

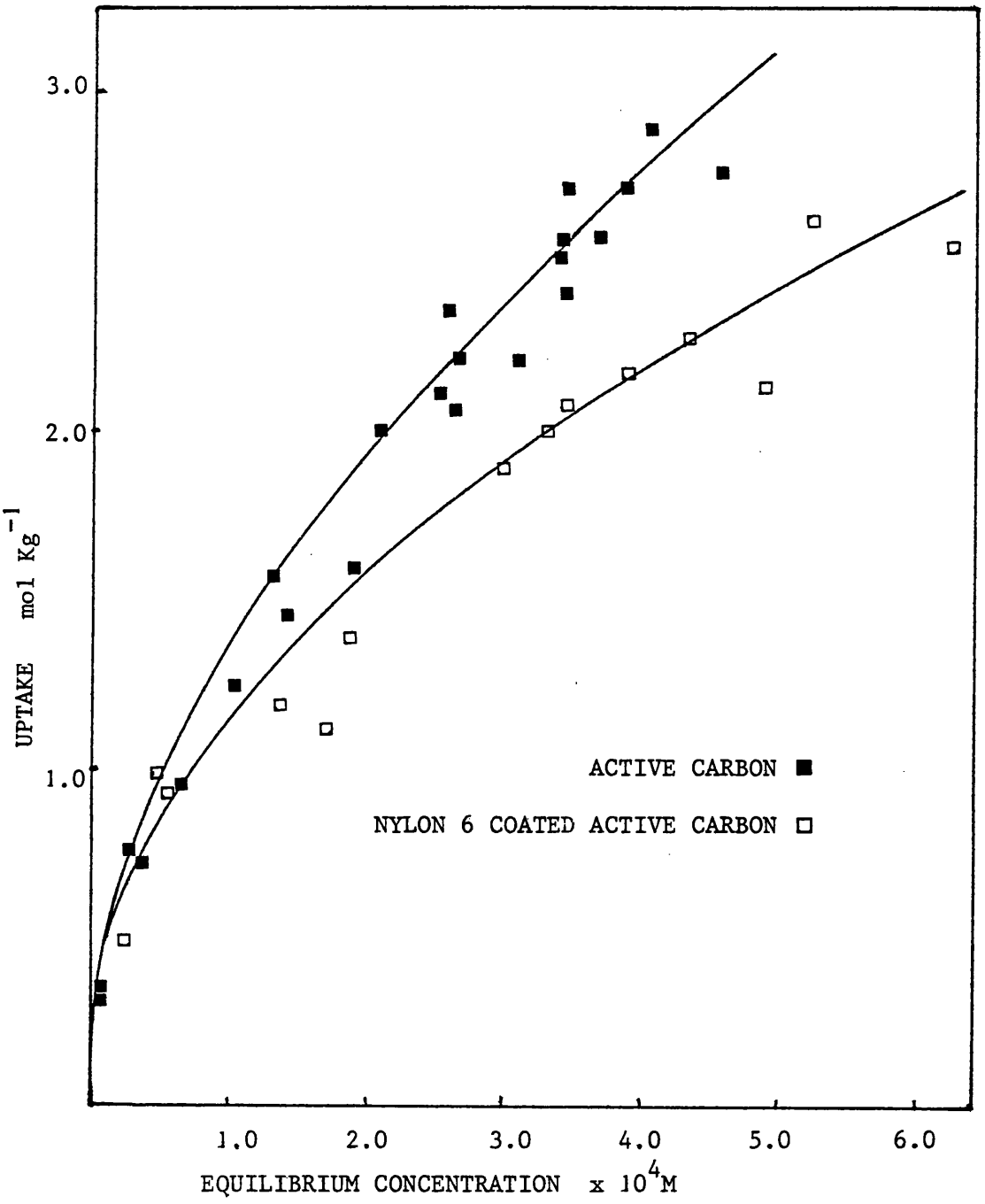


FIG 3.24 SORPTION ISOTHERMS FOR THE UPTAKE OF 4-METHOXYBENZOIC ACID ON TO UNCOATED AND NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

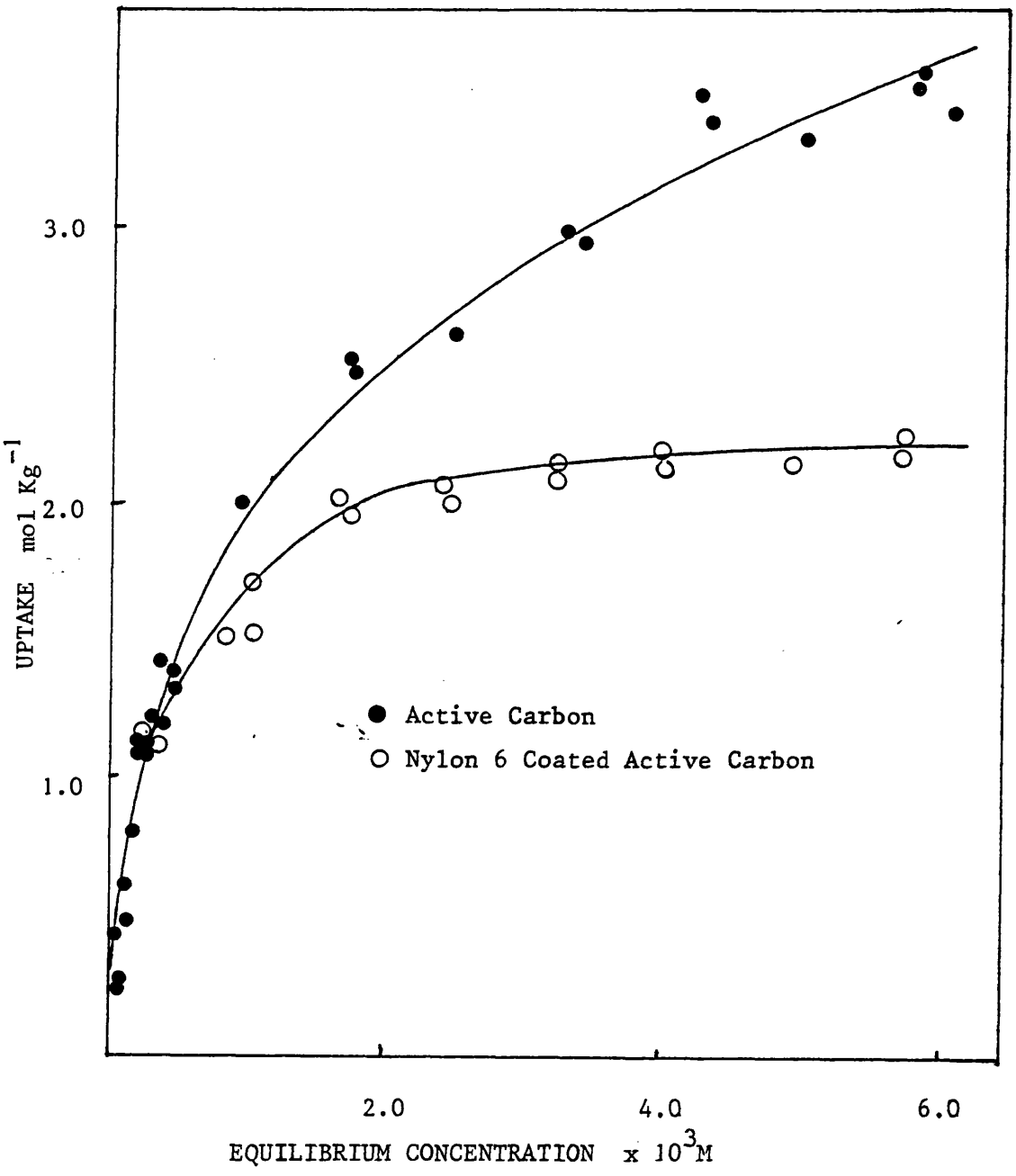


FIG 3.25 SORPTION ISOTHERMS OF ETHYL 4-AMINOBENZOATE BY UNCOATED AND NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AT 30°. INITIAL CONCENTRATION RANGE: 0 - 7 x 10^{-3} M

up to 5×10^{-2} M. The presence of the nylon 6 coat on the active carbon resulted in a lower uptake of 4-methoxybenzoic acid, 4-nitrophenol and ethyl 4-aminobenzoate, the latter showing the greatest degree of suppression.

Treatment of Results.

L type isotherms were analysed using the Freudlich, Langmuir and Radke equations shown in equations 1.2, 1.3, and 1.6 respectively.

$$n = aC_{eq}^{1/m} \quad \text{.....(1.2).}$$

$$n = \frac{n_{max}.b'.C_{eq}}{1 + b'C_{eq}} \quad \text{.....(1.3).}$$

$$n = \frac{\alpha C_{eq}}{1 + \frac{\alpha}{\beta} C_{eq}^{(1-\gamma)}} \quad \text{.....(1.6).}$$

To assess which equation best fitted the isotherm data for single solute sorption systems, the data was submitted to a computerised non-linear regression analysis (Metzler 1974, Appendix 1.). The regression analysis data gives the various constants of the equations together with their standard deviations. In addition, a correlation index statistic is supplied which is a measure of the degree of fit to a particular equation. This value is obtained by comparing the experimental uptake data with those obtained from the "best-fit" line for a given equilibrium concentration. The correlation index is the correlation coefficient for the plot of theoretical and experimental uptake values at given equilibrium concentrations and gives a value of 1.0 for an exact fit; values in excess of 0.950 can be considered to fit the data satisfactorily. Non-linear regression analysis data

for sorption on to uncoated and nylon 6 coated active carbon are given in tables 3.31, 3.32 and 3.33, for the Langmuir, Freudlich and Radke equations respectively. The Radke and Langmuir equations show high correlation indices for all four solutes on the uncoated sorbent indicating that both equations adequately fit the experimental data. The data for the 4-nitrophenol as fitted to the Freudlich equation, shows a low correlation index and degree of fit as would be expected because the isotherm is of L_2 type. The correlation index values for the nylon 6 coated sorbent showed a similar trend, although the numerical values were generally lower than for the uncoated systems. The equation which best fits the data obtained from sorption studies on nylon 6 coated active carbon is, therefore, not clear. As the sorption characteristics of the solutes from solution are not definitively described by any one of the three isotherm equations, full tables of uptake data are given in Appendix 2.

3.3.4 The Sorption of Solutes from Binary Solute Solution in Uncoated and Nylon 6 Coated Active Carbon.

The effects of competing species on the adsorption of the model solutes by both the uncoated and nylon 6 coated active carbon granules was assessed using the experimental method of Fritz and Schlunder (1974). A series of initial solutions were prepared covering a range of concentration of one solute (component 1) in the presence of a fixed concentration of a second solute (component 2). After equilibration, the concentration of both solutes in the supernatant solution was determined. Component 1 is, therefore, subjected to competition from a fixed initial concentration of component 2. The latter is subjected

Table 3.31 Adsorption Isotherm Data for the Model Adsorbates on to Active Carbon from Dilute Solution at 30° and pH2.32 (0.5 ionic strength) fitted to the Freudlich Equation.

Compound	a $dm^3\ Kg^{-1}$	Standard Deviation	m	Standard Deviation	Correlation Index
Uncoated Carbon					
4-nitrophenol	65.6	9.7	2.01	0.09	0.981
phenol	73.4	4.1	1.54	0.02	0.990
ethyl 4-aminobenzoate	26.7	1.9	2.59	0.08	0.991
4-methoxybenzoic acid	190.6	19.2	1.84	0.04	0.988
Nylon 6 Coated Carbon					
4-nitrophenol	8.8	0.5	5.01	0.31	0.933
ethyl 4-aminobenzoate	6.4	0.7	5.14	0.51	0.955
4-methoxybenzoic acid	89.4	16.6	2.09	0.10	0.973

Table 3.32 Adsorption Isotherm Data for the Model Adsorbates on to Active Carbon from Dilute Solution at pH2.32 (0.5M ionic strength) and 30° Fitted to the Langmuir Equation.

Compound	N_{max} (mol Kg^{-1})	Standard Deviation	b (dm^3 mol^{-1})	Standard Deviation	Correlation Index
4-nitrophenol	4.48	0.27	972.6	137.1	0.982
phenol	3.66	0.24	294.0	34.8	0.992
ethyl 4-aminobenzoate	3.81	0.11	1384.7	134.0	0.987
4-methoxybenzoic acid	4.24	0.33	4241.6	695.2	0.984
Nylon 6 Coated Carbon					
4-nitrophenol	4.27	0.13	954.3	106.3	0.961
ethyl 4-aminobenzoate	2.31	0.05	3601.9	344.3	0.961
4-methoxybenzoic acid	3.31	0.34	4738.6	1139.4	0.957

Table 3.33 Adsorption Isotherm Data for the Model Adsorbates on Active Carbon from Dilute Solution at pH2.32 (0.5M ionic strength) and 30° Fitted to the Radke Equation.

Solute	α $dm^3\ Kg^{-1}$	Standard Deviation	β	Standard Deviation	γ	Standard Deviation	Correlation Index
Uncoated Carbon							
4-nitrophenol	9231.7	287.8	26.35	9.88	0.320	0.069	0.984
phenol	1078.98	50.9	3.79	0.20	0.007	0.003	0.992
ethyl 4-amino-benzoate	8665.49	757.13	9.80	0.76	0.186	0.015	0.992
4-methoxybenzoic acid	18075.70	1992.10	4.36	0.38	0.004	0.0005	0.984
Nylon 6 Coated Carbon							
4-nitrophenol	12222.4	1284.8	7.07	0.26	0.14	0.006	0.984
ethyl 4-amino-benzoate	23347.0	3533.06	4.71	0.37	0.01	0.01	0.962
4-methoxybenzoic acid	23039.6	4771.32	11.11	2.07	0.18	0.02	0.962

to competition from the range of initial concentration of component 1. Initially the sorption of binary solute mixtures of phenol and 4-nitrophenol on uncoated active carbon were studied. The sorption from several different binary solute mixtures involving the other model solutes was then studied on both the uncoated and nylon 6 coated adsorbents.

Treatment of Results.

The sorption of component 1, for each binary solute mixture, was calculated and is plotted as an adsorption isotherm. A competitive sorption effect is shown by an overall lowering of the adsorption isotherm relative to that obtained in the absence of competition.

The sorption of component 2 was also calculated and the data is plotted as uptake versus the initial concentration of component 1. As the amount of component 2 in the system is constant, a competitive sorption effect is shown by a reduction in the uptake of component 2 as the total amount of component 1, represented by the initial solution concentration, is increased. The uptake of component 2 at zero concentration of component 1 is the single solute uptake corresponding to the given initial concentration of component 2. Although the data shown on these single point plots are scattered due to a number of variables in the system not taken into account by the representation, a general linear trend is evident in certain systems. The data from the single point plots was therefore submitted to a computerised linear regression analysis to estimate whether competitive sorption was present with respect to the constant concentration component. The criteria used to determine whether competitive sorption was present were as follows. If the value of the slope was less than

the standard deviation i.e. the coefficient of variation exceeded 100% and the correlation coefficient was less than 0.5; competitive sorption was taken not to be occuring. If the value of the slope exceeded the value of its standard deviation i.e. the coefficient of variation was lower than 100% and the correlation coefficient exceeded 0.5 competitive sorption was deemed to be occuring.

3.3.4.1 The Sorption of 4-nitrophenol : phenol Mixtures by Uncoated Active Carbon.

The uptake of phenol over the concentration range 0 - $6x10^{-3}$ M was determined in the presence of $1x10^{-3}$ M, $3x10^{-3}$ M and $5x10^{-3}$ M 4-nitrophenol the results are shown in figures 3.26 and 3.27. The sorption isotherms for phenol were L_1 type in nature and were lowered in the presence of 4-nitrophenol, the degree of suppression increasing as the concentration of competitor increased.

The corresponding single point plots for 4-nitrophenol are shown in figure 3.27. It can be seen that phenol has no effect on the adsorption of 4-nitrophenol (Table 3.34).

The uptake of 4-nitrophenol over the concentration range 0 - $1x10^{-3}$ M was determined in the presence of $5x10^{-3}$ M phenol which is shown in figures 3.28 and 3.29. The sorption isotherm for 4-nitrophenol is superimposed upon its single solute isotherm, both of which are L_1 type in nature. The uptake of phenol (initial concentration $5x10^{-3}$ M) is clearly suppressed by 4-nitrophenol which is shown in the single point plot (figure 3.29, table 3.34).

3.3.4.2 The Sorption of 4-methoxybenzoic acid : 4-nitrophenol Mixtures by Coated and Uncoated Active Carbon.

The uptake of 4-methoxybenzoic acid on uncoated active carbon and

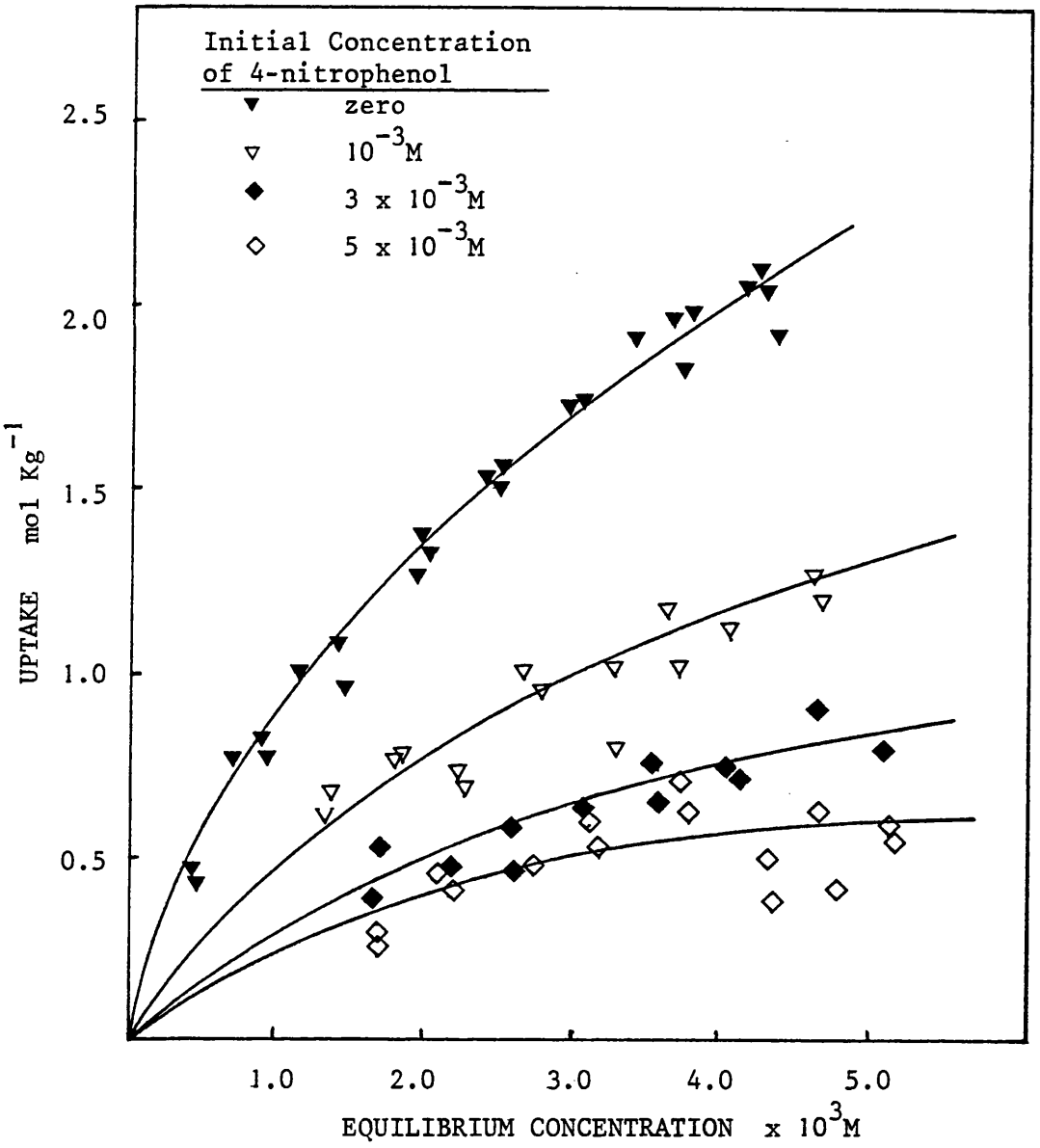


FIG 3.26 SORPTION ISOTHERMS FOR PHENOL BY ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-NITROPHENOL. INITIAL PHENOL CONCENTRATION 0 - 6 x 10^{-3}M

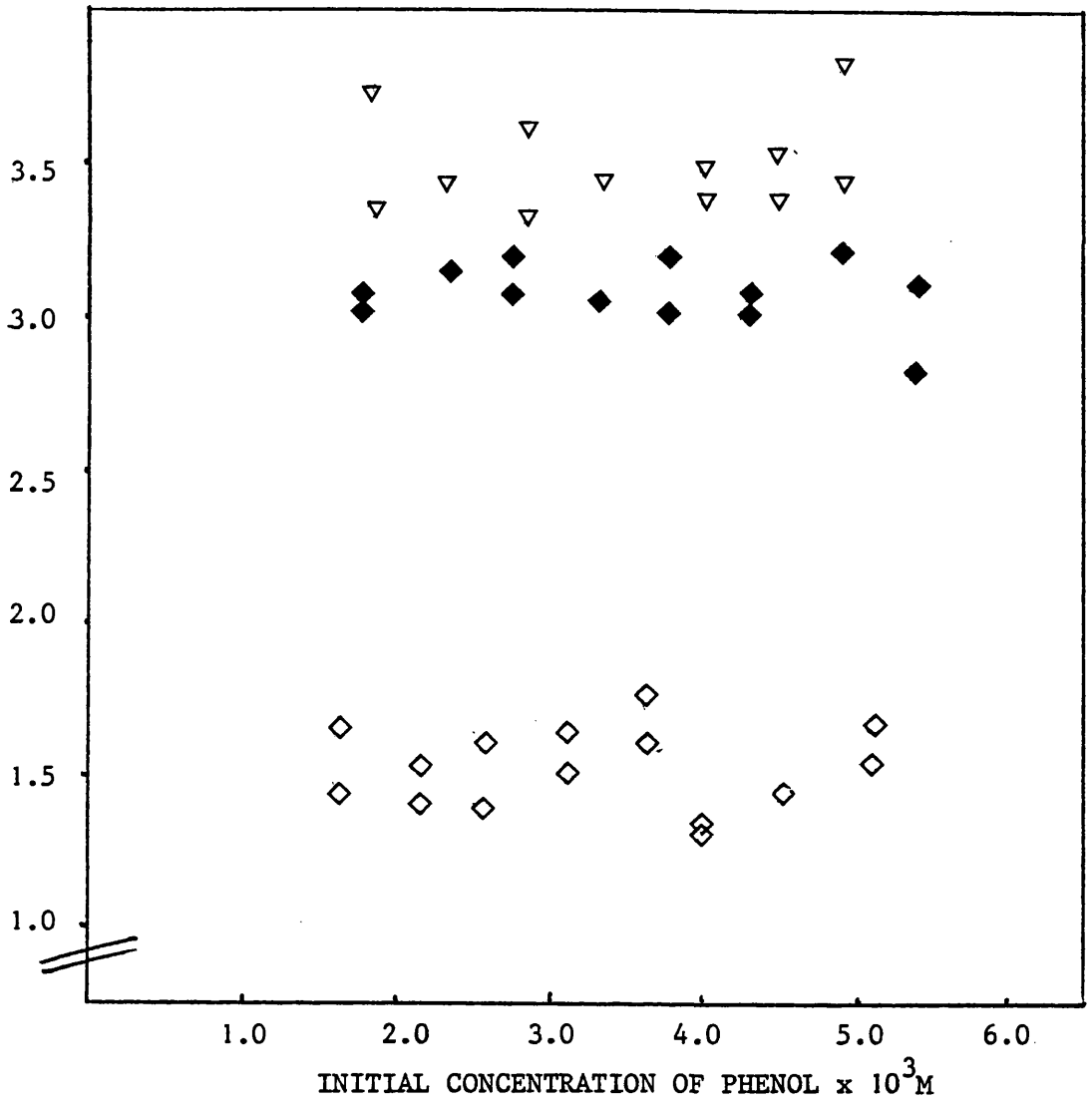


FIG 3.27 : MIXED SORPTION SINGLE POINT PLOT FOR 4-NITROPHENOL ON TO ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF PHENOL.

4-NITROPHENOL INITIAL CONCENTRATION: ▽ $5x10^{-3}$M , ◆ $3x10^{-3}$M, ◇ 10^{-3}M

Table 3.34 Data from the Statistical Analysis of the Single Point Plot of the Phenol : 4-nitrophenol Binary Solute System at pH2.32 (0.5M ionic strength) and 30^{o}.

Solute	Competitor	Initial Concentration Ratio;Solute : Competitor	Slope mol Kg^{-1} M^{-1}	Standard Deviation	Coefficient of Variation	Correlation Coefficient
4-nitrophenol	phenol	5 : 5	-44.91	51.69	-114.9%	0.23
		3 : 5	11.46	19.79	172.4%	0.37
		1 : 5	8.54	33.54	400.0%	0.07
phenol	4-nitrophenol	5 : 1	-0.81	0.08	-9.4%	0.94

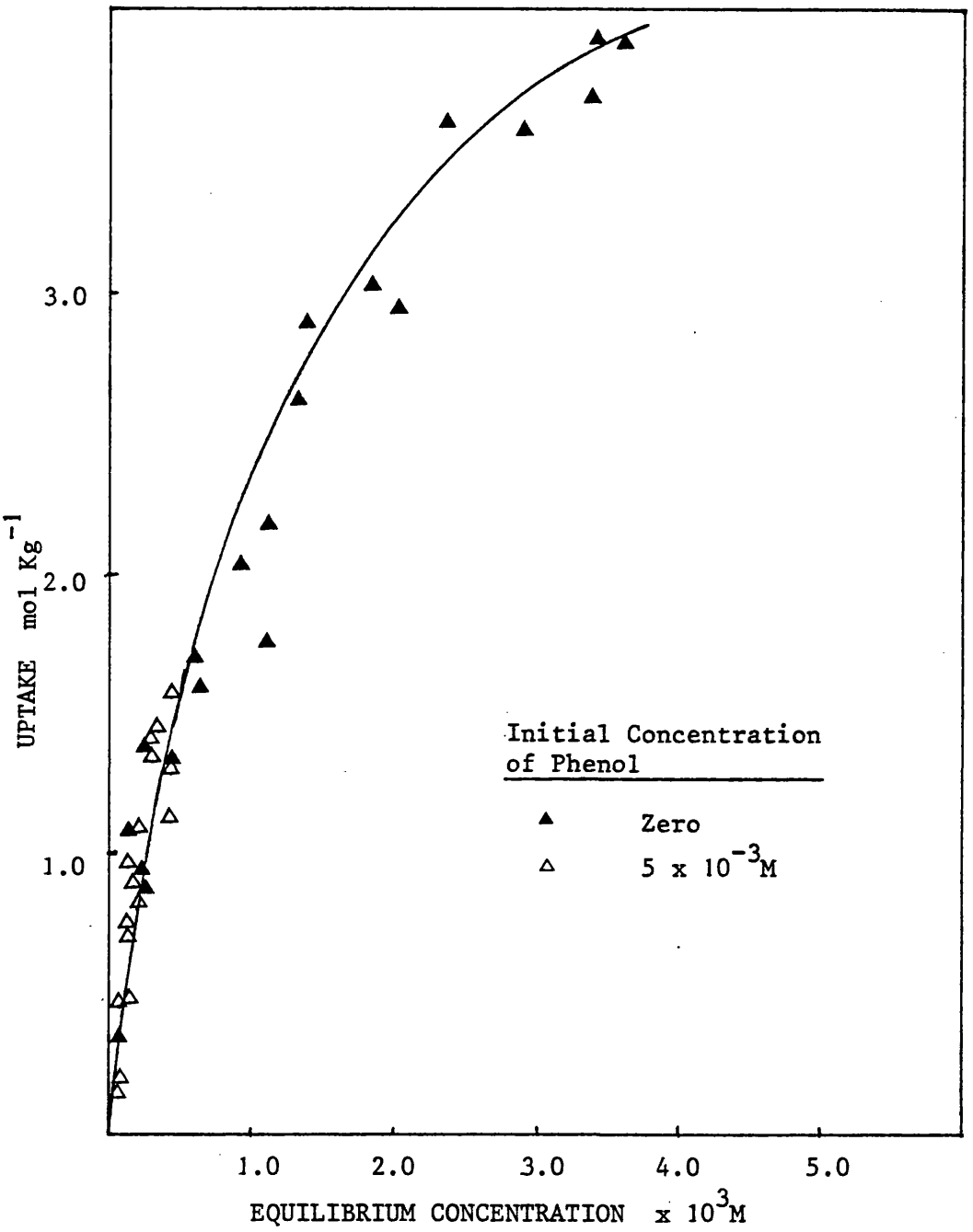


FIG 3.28 SORPTION ISOTHERMS FOR 4-NITROPHENOL BY ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF PHENOL INITIAL CONCENTRATION 0 - 5 x 10^{-3}M.

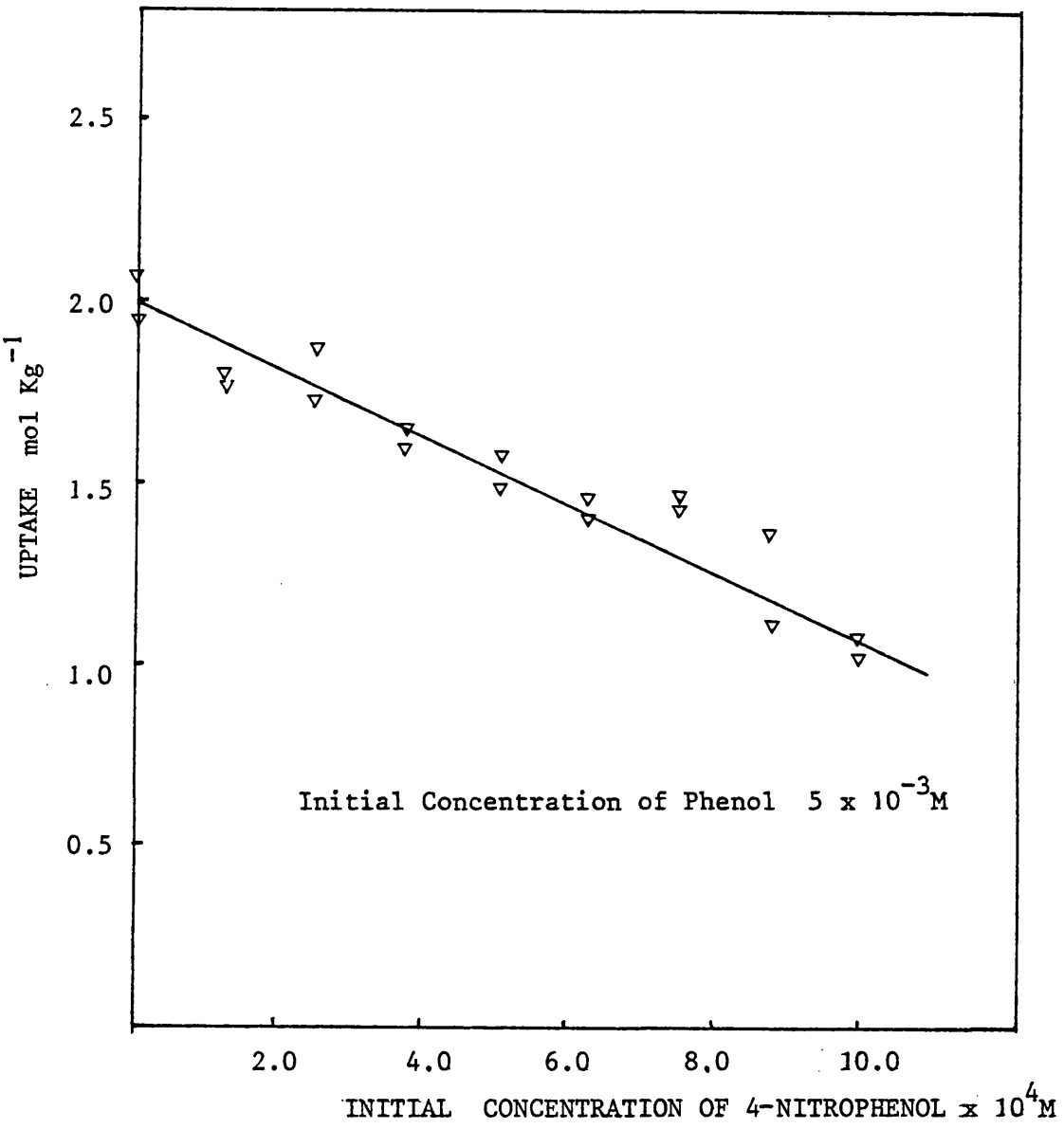


FIG 3.29 MIXED SORPTION SINGLE POINT PLOT OF PHENOL ON TO ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-NITROPHENOL. INITIAL CONCENTRATION 0 - 10^{-3}M.

the concentration range 0 - $1x10^{-3}$ M was determined in the presence of $1x10^{-3}$ M, $3x10^{-3}$ M and $5x10^{-3}$ M 4-nitrophenol. The sorption isotherms of 4-methoxybenzoic acid were all of the L_2 type (figure 3.30) and uptake was suppressed in the presence of an increasing concentration of 4-nitrophenol. The corresponding single point plot for the 4-nitrophenol uptake in this system (figure 3.31) shows that 4-methoxybenzoic acid is capable of suppressing the uptake of 4-nitrophenol (table 3.35).

The uptake of 4-methoxybenzoic acid on nylon 6 coated carbon, over the same concentration range, in the presence of $5x10^{-3}$ M 4-nitrophenol is shown in figure 3.32, where a similar pattern of competition occurs on the coated sorbent as on the uncoated carbon. The corresponding single point plot of 4-nitrophenol (figure 3.33) indicates that, although the data is scattered, sorption of 4-nitrophenol is suppressed with respect to its single solute uptake but is apparently independent of increasing competitor concentration. (table 3.35).

3.3.4.3 The Sorption of Ethyl 4-aminobenzoate : 4-methoxybenzoic acid Mixtures by Coated and Uncoated Carbon.

The sorption isotherms of 4-methoxybenzoic acid on uncoated active carbon over the concentration range 0 - $1x10^{-3}$ M in the presence of $1x10^{-3}$ M, $3x10^{-3}$ M and $5x10^{-3}$ M ethyl 4-aminobenzoate are shown in figure 3.34. The sorption of 4-methoxybenzoic acid is suppressed by ethyl 4-aminobenzoate and, as before, the extent of suppression increases with increasing competitor concentration. The isotherm of 4-methoxybenzoic acid changes from L_1 to C_1 to S_1 as the competitor concentration increases from 10^{-3} M to $3x10^{-3}$ M to $5x10^{-3}$ M respectively.

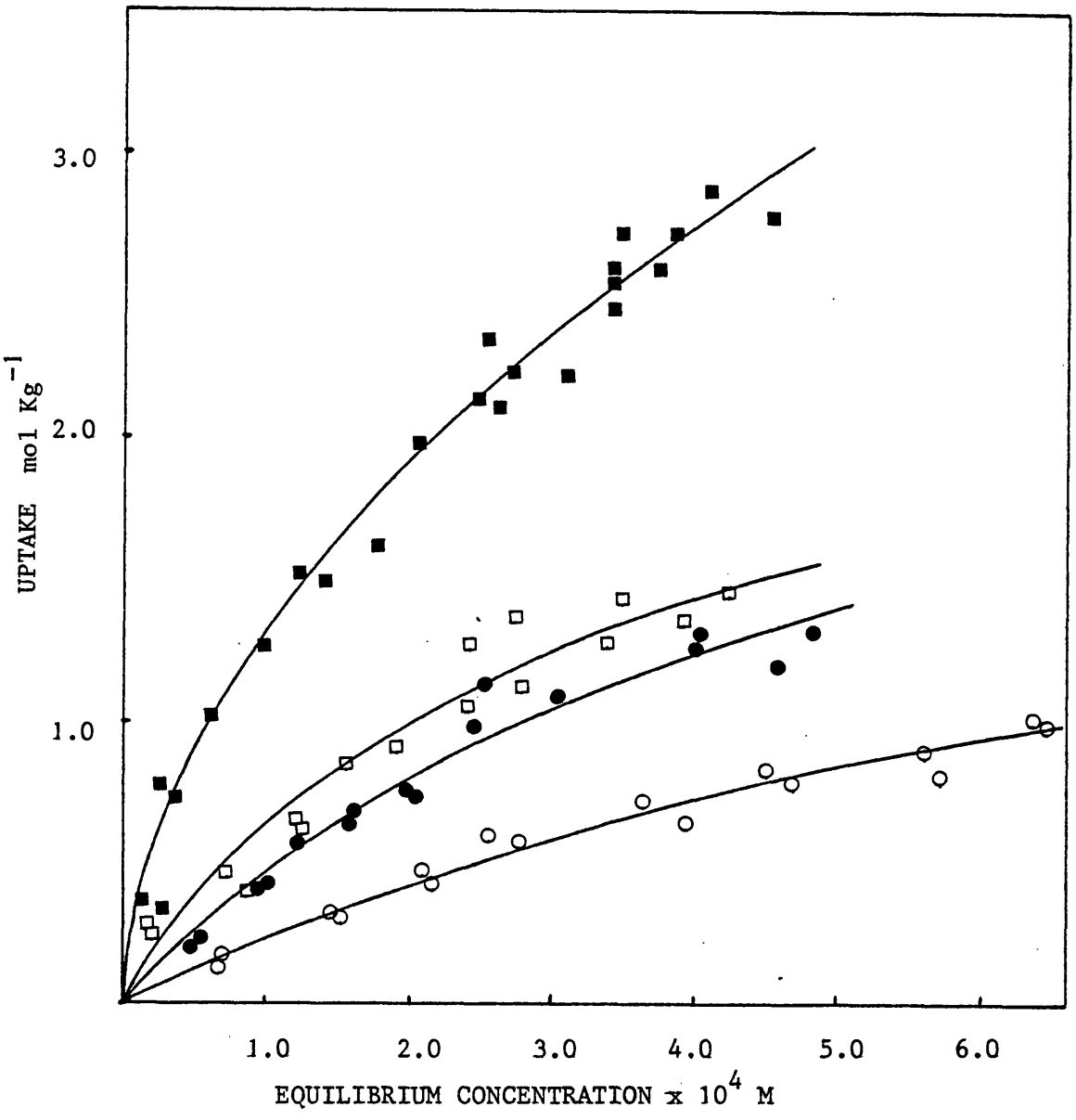


FIG 3.30 SORPTION ISOTHERMS FOR 4-METHOXYBENZOIC ACID ON TO ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-NITROPHENOL. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

4-NITROPHENOL INITIAL CONCENTRATION ■ Zero □ 5 x 10^{-3}M ● 3 x 10^{-3}M ○ 10^{-3}M

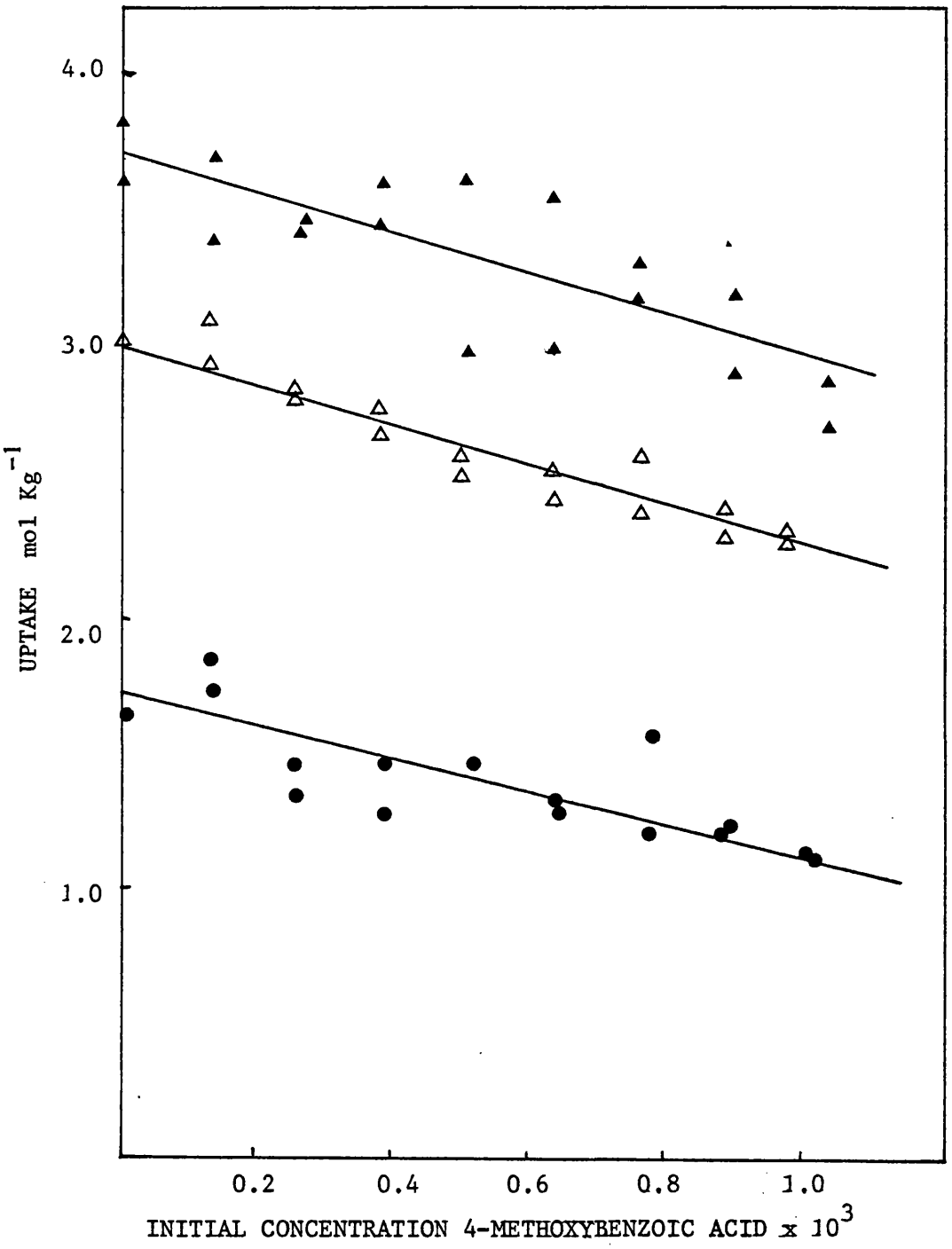


FIG 3.31 MIXED SORPTION SINGLE POINT PLOT FOR 4-NITROPHENOL ON TO ACTIVE CARBON AT pH 2.32(0.5M IONIC STRENGTH) AND 30^{o} IN THE PRESENCE OF 4-METHOXYBENZOIC ACID

INITIAL CONCENTRATION 4-NITROPHENOL: ▲-5 x 10^{-3}M, △-3 x 10^{-3}M, ●-10^{-3}M

Table 3.35 Data from the Statistical Analysis of the Single Point Plot for the Sorption of 4-nitrophenol in the Presence of 4-methoxybenzoic acid on to Uncoated and Nylon 6 Coated Active Carbon of pH 2.32 (0.5M ionic strength) and 30°.

Initial Concentration Ratio 4-nitrophenol : 4-methoxybenzoic acid	Sorbent	Slope mol $Kg^{-1}M^{-1}$	Standard Deviation	Coefficient of Variation	Correlation Coefficient
1:1	Uncoated	- 539.4	123.8	- 22.9	0.76
3:1	Uncoated	- 804.9	73.9	- 9.2	0.95
5:1	Uncoated	- 720.0	185.7	- 25.8	0.72
5:1	Nylon 6 Coated	- 72.6	162.6	-222.2	0.12

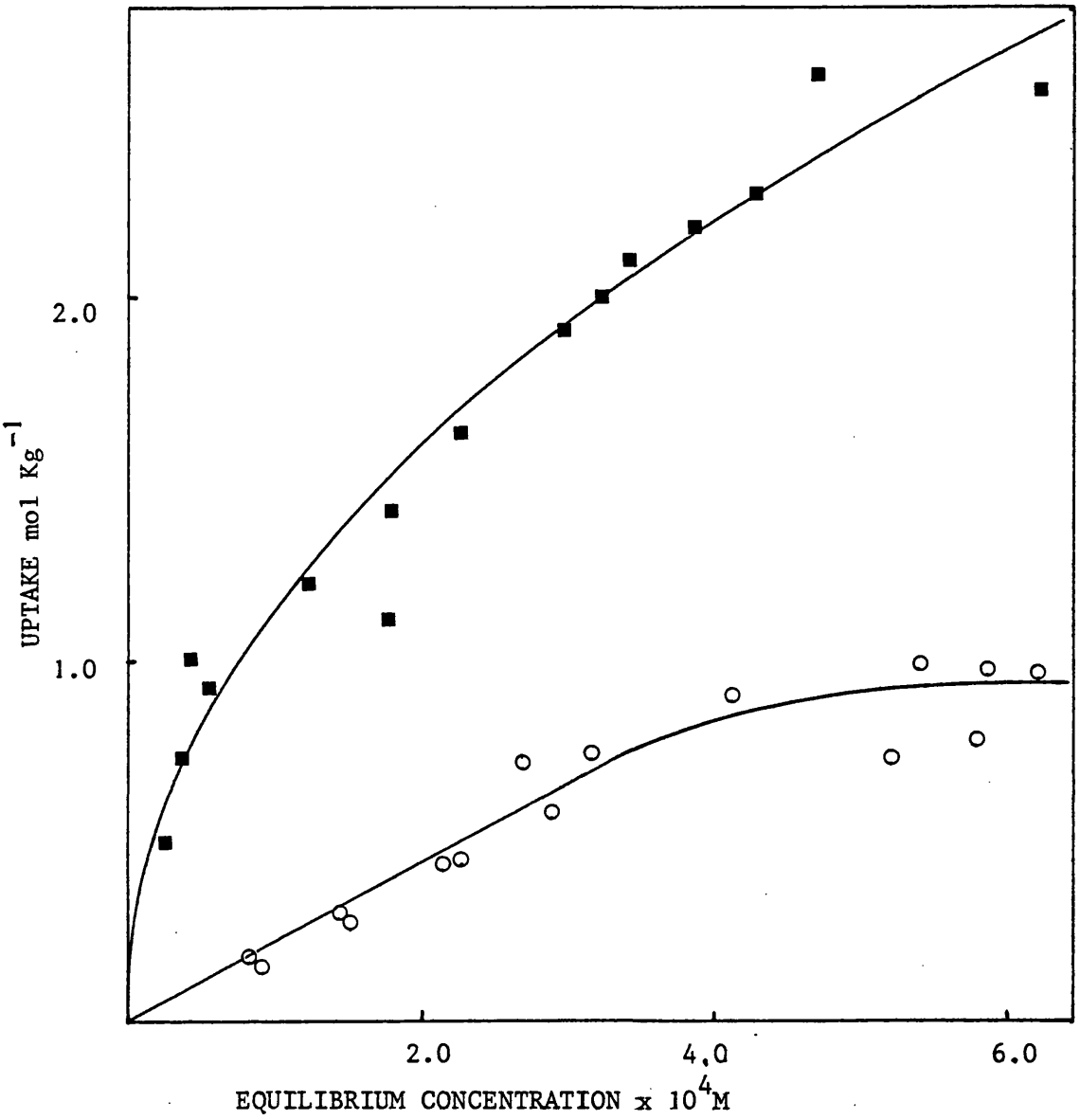


FIG 3.32 SORPTION ISOTHERMS FOR 4-METHOXYBENZOIC ACID ON TO NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-NITROPHENOL. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

INITIAL CONCENTRATION 4-NITROPHENOL: ■-ZERO ; ○-5 x 10^{-3}M

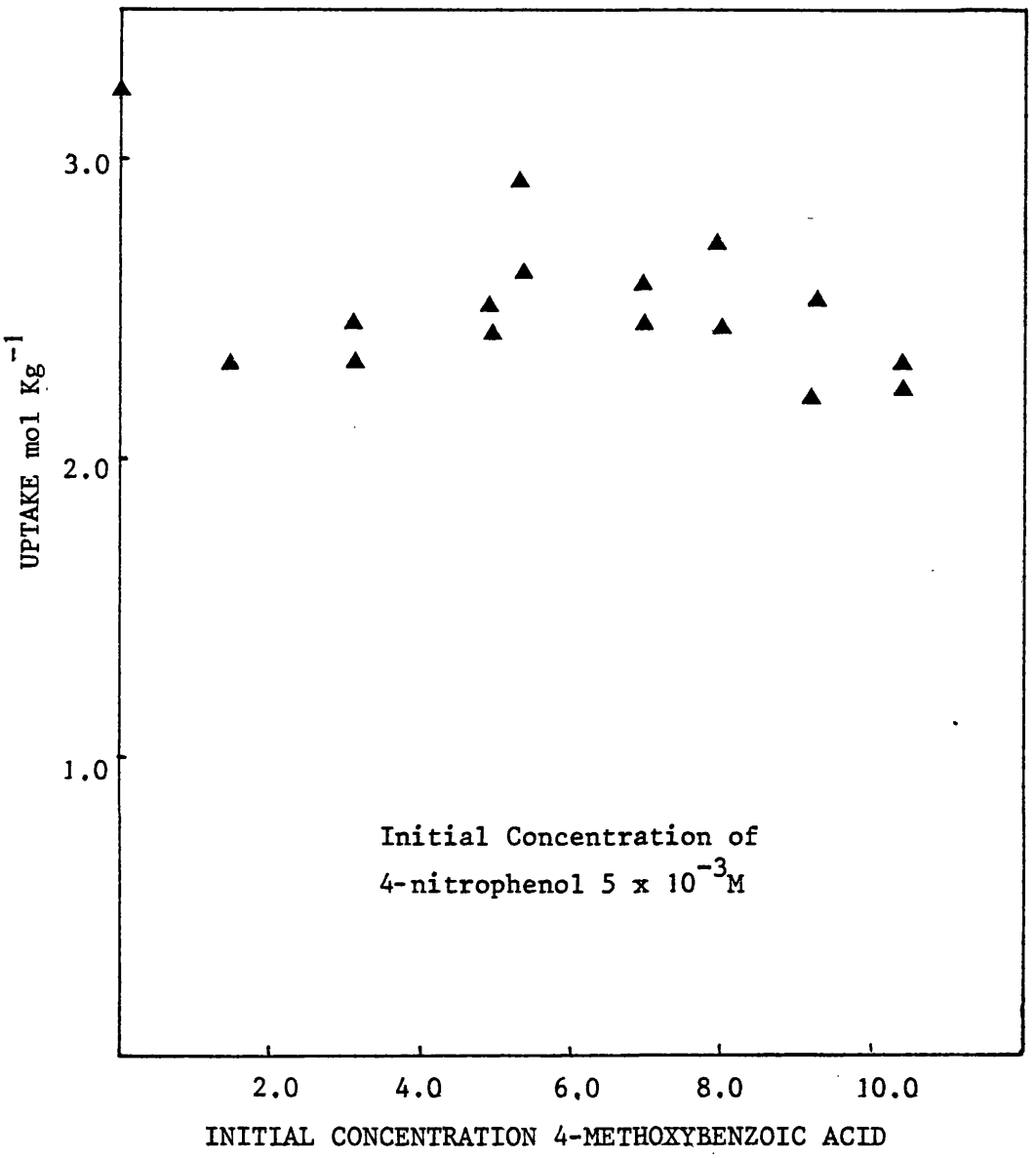


FIG 3.33 MIXED SORPTION SINGLE POINT PLOT FOR 4-NITROPHENOL ON TO NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-METHOXYBENZOIC ACID.

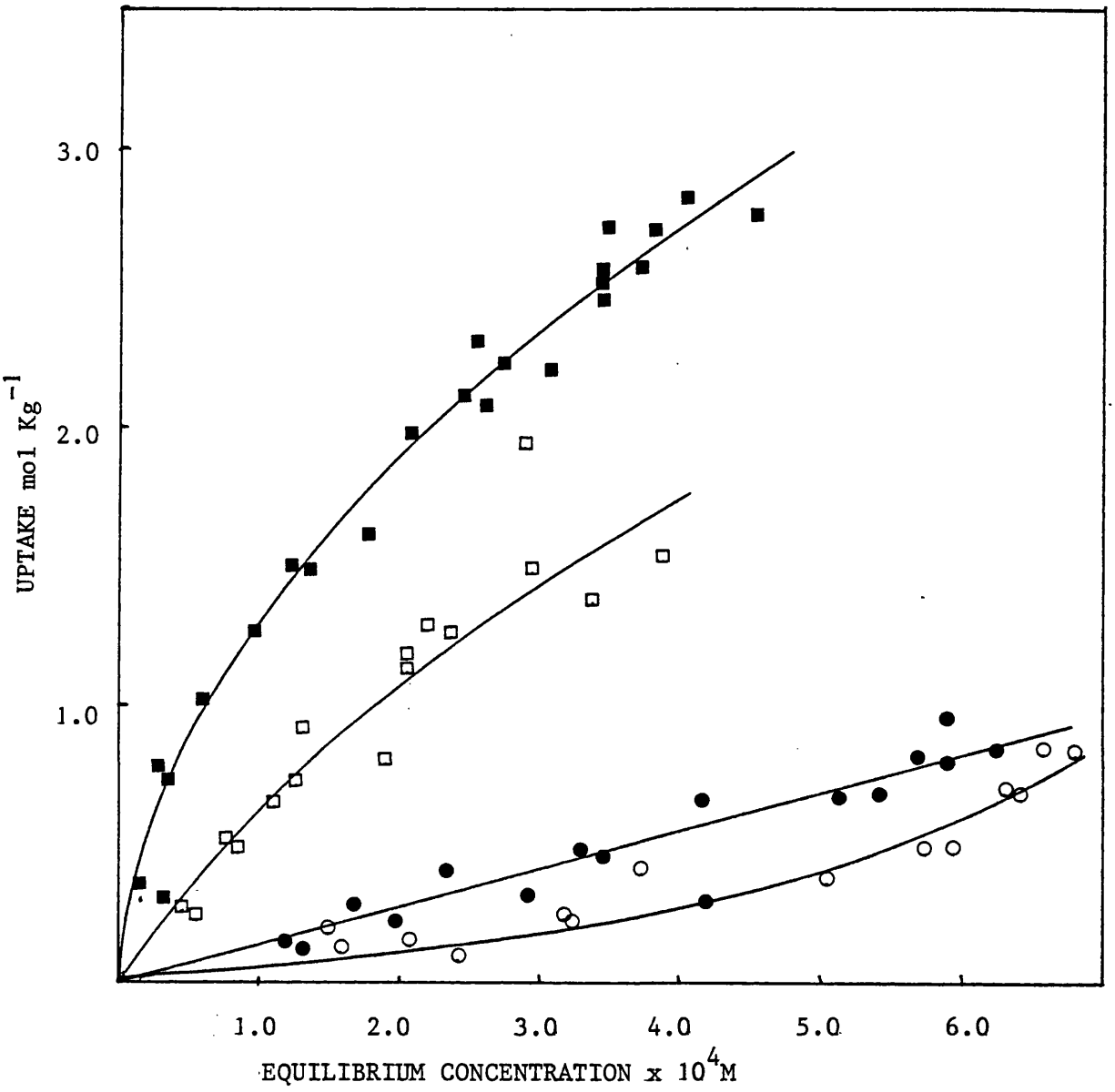


FIG 3.34 SORPTION ISOTHERMS FOR 4-METHOXYBENZOIC ACID ON TO ACTIVE CARBON AT pH 2.32(0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF ETHYL 4-AMINOBENZOATE. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

INITIAL CONCENTRATION ETHYL 4-AMINOBENZOATE: ■ — ZERO; □ — 5 x 10^{-3}M ● — 3 x 10^{-3}M ; ○ — 10^{-3}M.

The corresponding single point plot for ethyl 4-aminobenzoate (figure 3.30) shows that 4-methoxybenzoic acid suppresses the uptake of ethyl 4-aminobenzoate, the degree of suppression apparently decreasing as the concentration of ethyl 4-aminobenzoate decreases (table 3.36). The sorption isotherm of 4-methoxybenzoic acid on nylon 6 coated carbon over the same range of initial concentration in the presence of $5x10^{-3}$ M ethyl 4-aminobenzoate is S_1 type in nature (figure 3.36) indicating that the competitive nature of the two solutes is similar to that on the uncoated material. In contrast to the uncoated carbon system, the corresponding uptake of $5x10^{-3}$ M initial concentration ethyl 4-aminobenzoate is apparently unaffected by the presence of 4-methoxybenzoic acid (figure 3.37, table 3.36).

3.3.4.4. The Sorption of Ethyl 4-aminobenzoate : 4-nitrophenol Mixtures by Coated and Uncoated Carbon.

The sorption isotherms of 4-nitrophenol on uncoated active carbon over the concentration range 0 - $4x10^{-3}$ M in the presence of $3x10^{-3}$ M and $5x10^{-3}$ M ethyl 4-aminobenzoate are shown in figure 3.38. The isotherms indicate that a concentration dependent suppression of 4-nitrophenol uptake is taking place in this system. The single point plots for the uptake of ethyl 4-aminobenzoate show that a concentration dependent suppression of uptake is taking place in the presence of 4-nitrophenol (figure 3.39, table 3.37).

The sorption isotherm of 4-nitrophenol, on the coated sorbent, over the same concentration range in the presence of ethyl 4-aminobenzoate (initial concentration $5x10^{-3}$ M) is shown in figure 3.40 where it can be seen that competition is still apparent after application of the coat. The single point plot of ethyl 4-aminobenzoate, shown in figure 3.41 indicates that the sorption equilibrium is also

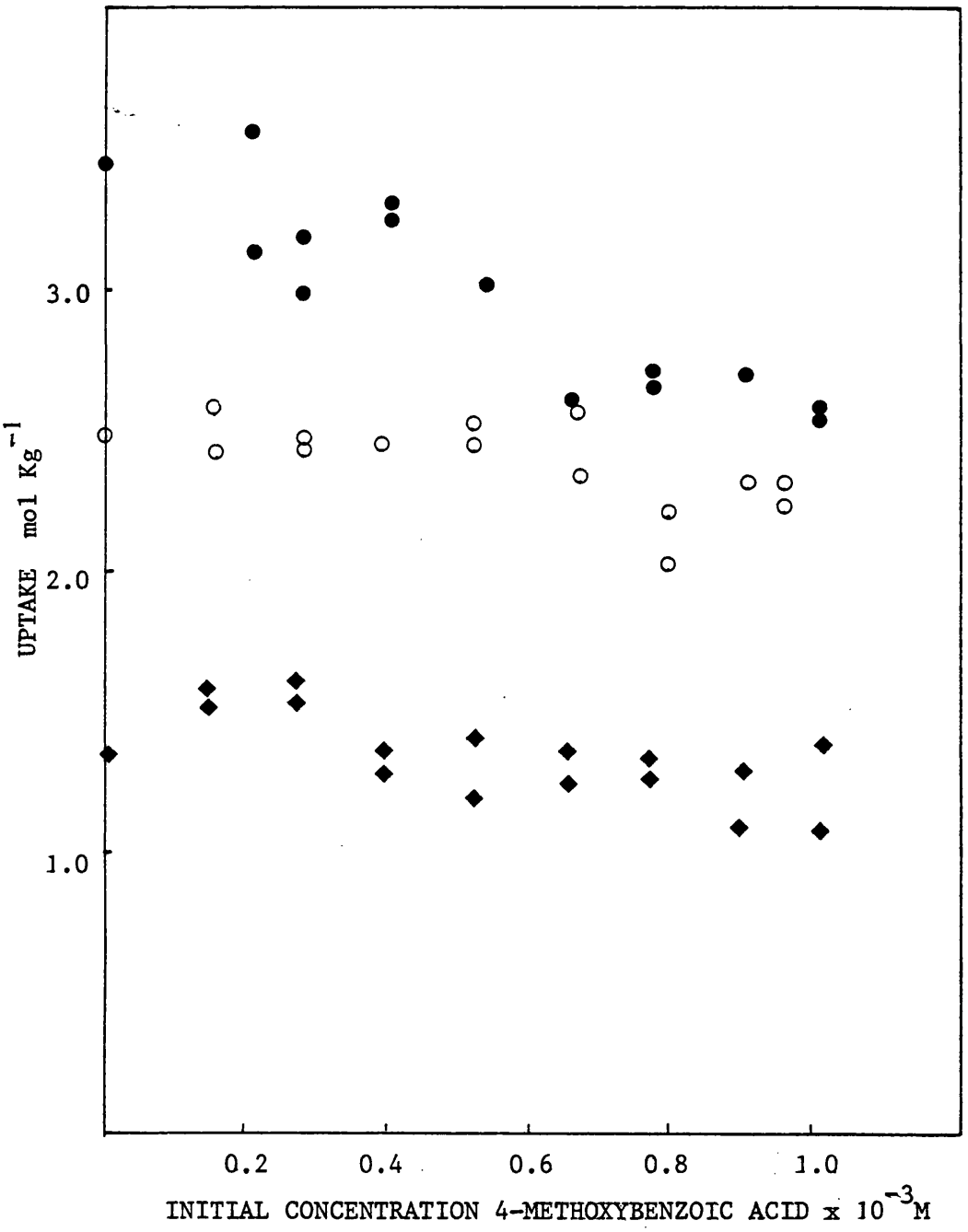


FIG 3.35 MIXED SORPTION SINGLE POINT PLOT FOR ETHYL 4-AMINOBENZOATE ON TO ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-METHOXYBENZOIC ACID

INITIAL CONCENTRATION ETHYL 4-AMINOBENZOATE; ●-5 x 10^{-3}M ; ○-3 x 10^{-3}M ◆-10^{-3}M

Table 3.36 Data from the Statistical Analysis of the Single Point Plot for the Sorption of Ethyl 4-aminobenzoate in the Presence of 4-methoxybenzoic acid on to Uncoated and Nylon 6 Coated Active Carbon at pH2.32 (0.5M ionic strength) and 30^{o}.

Initial Concentration Ratio Ethyl 4-aminobenzoate - 4-methoxybenzoic acid	Sorbent	Slope $mol\ Kg^{-1}\ M^{-1}$	Standard Deviation	Coefficient of Variation	Correlation Coefficient
1 : 1	Uncoated	-403.9	101.1	-25.1	0.73
3 : 1	Uncoated	-456.1	151.6	-33.2	0.63
5 : 1	Uncoated	-1108.0	181.9	-16.4	0.87
5 : 1	Nylon 6 Coated	-114.0	130.7	-114.9	0.24

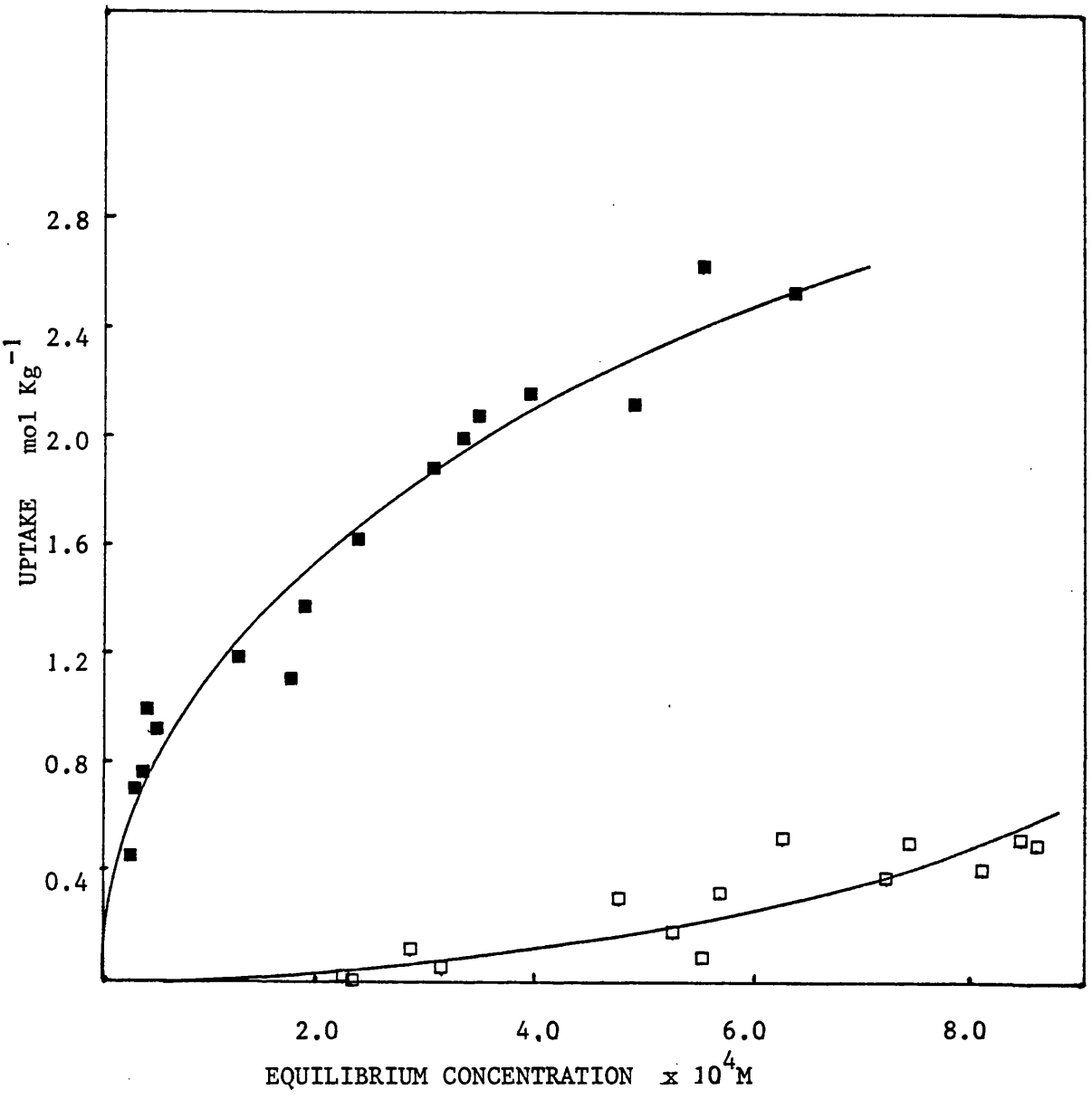


FIG 3.36 SORPTION ISOTHERMS FOR 4-METHOXYBENZOIC ACID ON TO NYLON 6 ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} IN THE PRESENCE OF ETHYL 4-AMINOBENZOATE. INITIAL CONCENTRATION RANGE 0 - 10^{-3}M

INITIAL CONCENTRATION ETHYL 4-AMINOBENZOATE: ■-ZERO ; □—5 x 10^{-3}M

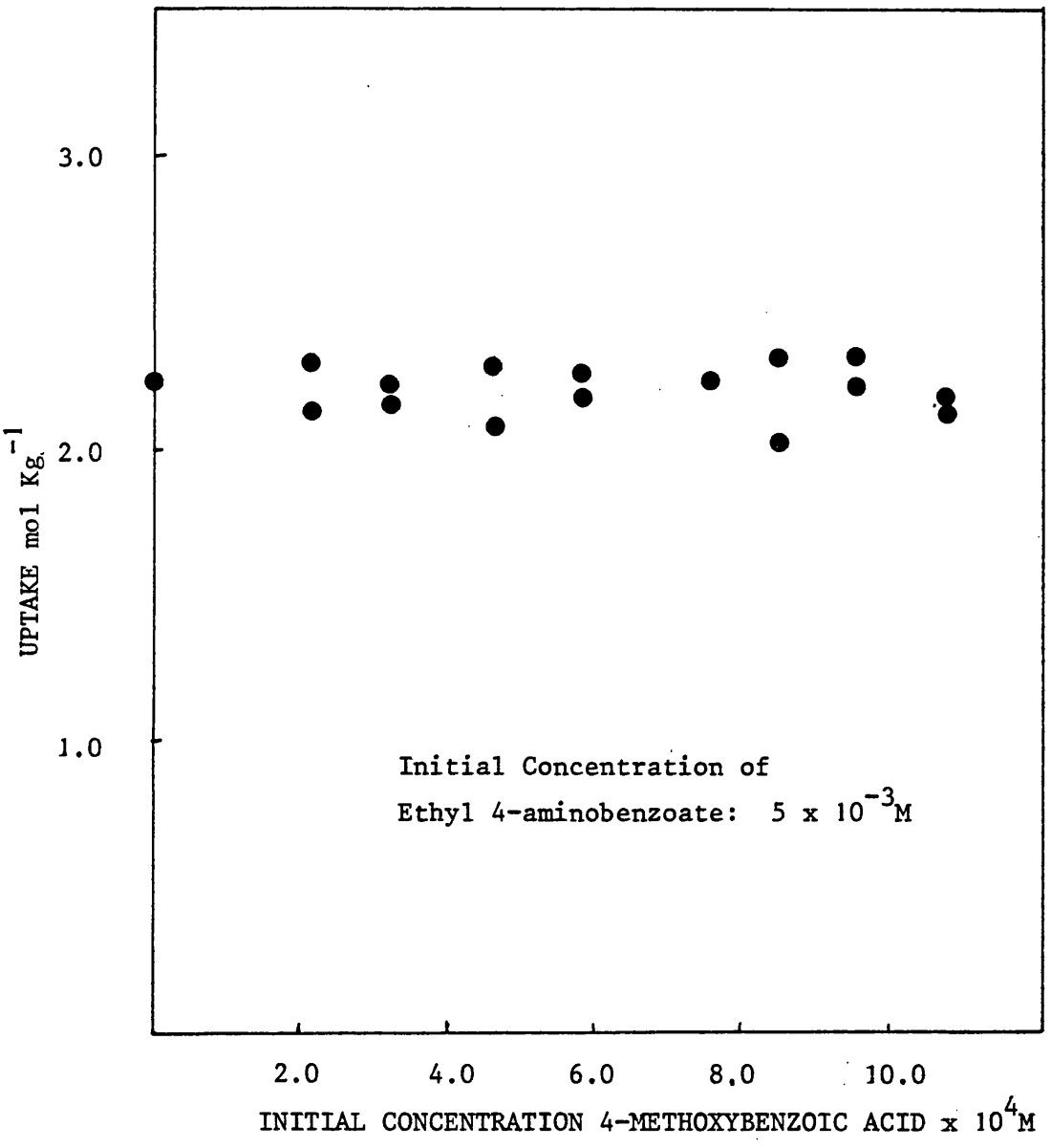


FIG 3.37 MIXED SORPTION SINGLE POINT PLOT FOR ETHYL 4-AMINOBENZOATE ON TO NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{0} IN THE PRESENCE OF 4-METHOXYBENZOIC ACID

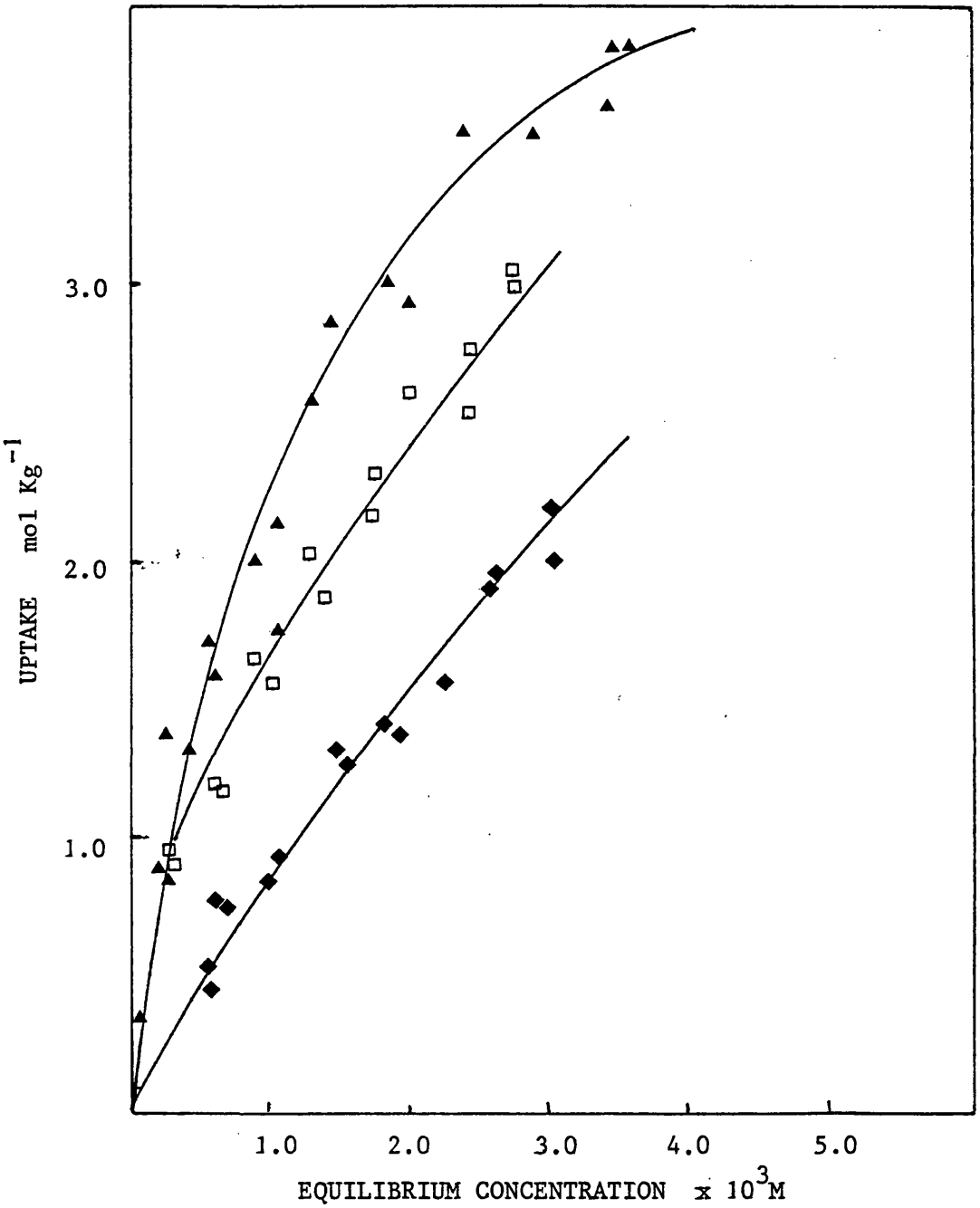


FIG 3.38 SORPTION ISOTHERMS FOR 4-NITROPHENOL ON TO ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} IN THE PRESENCE OF ETHYL-4-AMINOBENZOATE. INITIAL CONCENTRATION RANGE 0 - 4 x 10^{-3}M

INITIAL CONCENTRATION, ETHYL 4-AMINOBENZOATE: ▲-ZERO; □-5 x 10^{-3}M ◆-3 x 10^{-3}M

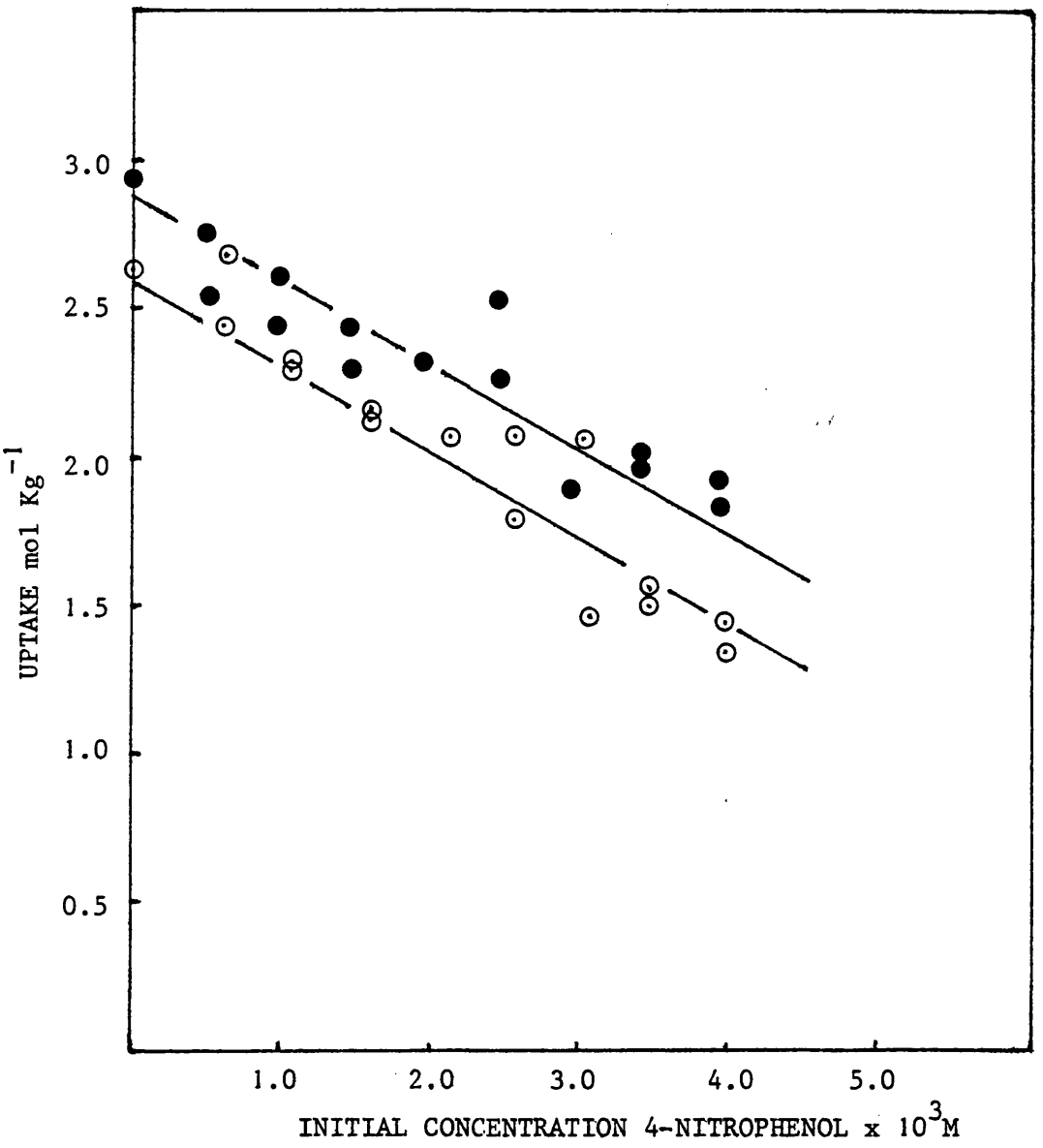


FIG 3.39 MIXED SORPTION SINGLE POINT PLOT FOR ETHYL 4-AMINO-BENZOATE ON TO ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF 4-NITROPHENOL

INITIAL CONCENTRATION, ETHYL 4-AMINOBENZOATE ● 5 x 10^{-3}M, ⊙ 3 x 10^{-3}M

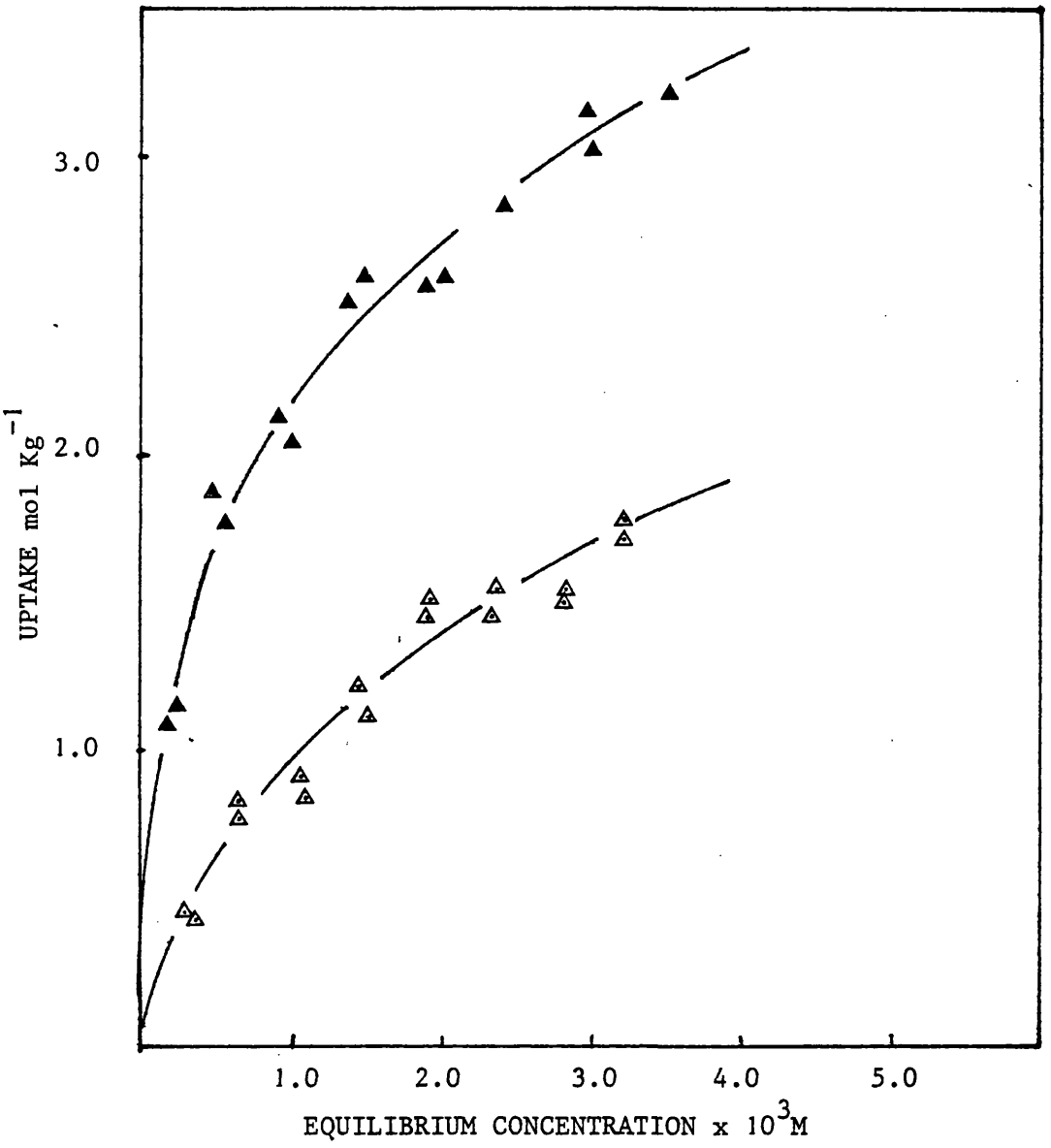


FIG 3.40 SORPTION ISOTHERMS FOR 4-NITROPHENOL ON TO NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° IN THE PRESENCE OF ETHYL 4-AMINOBENZOATE.

INITIAL CONCENTRATION, ETHYL 4-AMINOBENZOATE: ▲ ZERO △ 5 x 10^{-3}M

Table 3.37 Data from the Statistical Analysis of the Single Point Plots of Ethyl 4-aminobenzoate on to Uncoated and Nylon 6 Coated Active Carbon in the Presence of 4-nitrophenol at pH2.32 (0.5M ionic strength) and 30°.

Initial Concentration Ratio ;Ethyl 4-aminobenzoate : 4-nitrophenol	Sorbent	Slope mol Kg^{-1} M^{-1}	Standard Deviation	Coefficient of Variation	Correlation Coefficient
3 : 4	Uncoated	-330.3	46.2	-14.0	0.89
5 : 4	Uncoated	-213.4	70.3	-33.0	0.64
5 : 4	Nylon 6 coated	- 90.8	58.5	-64.5	0.38

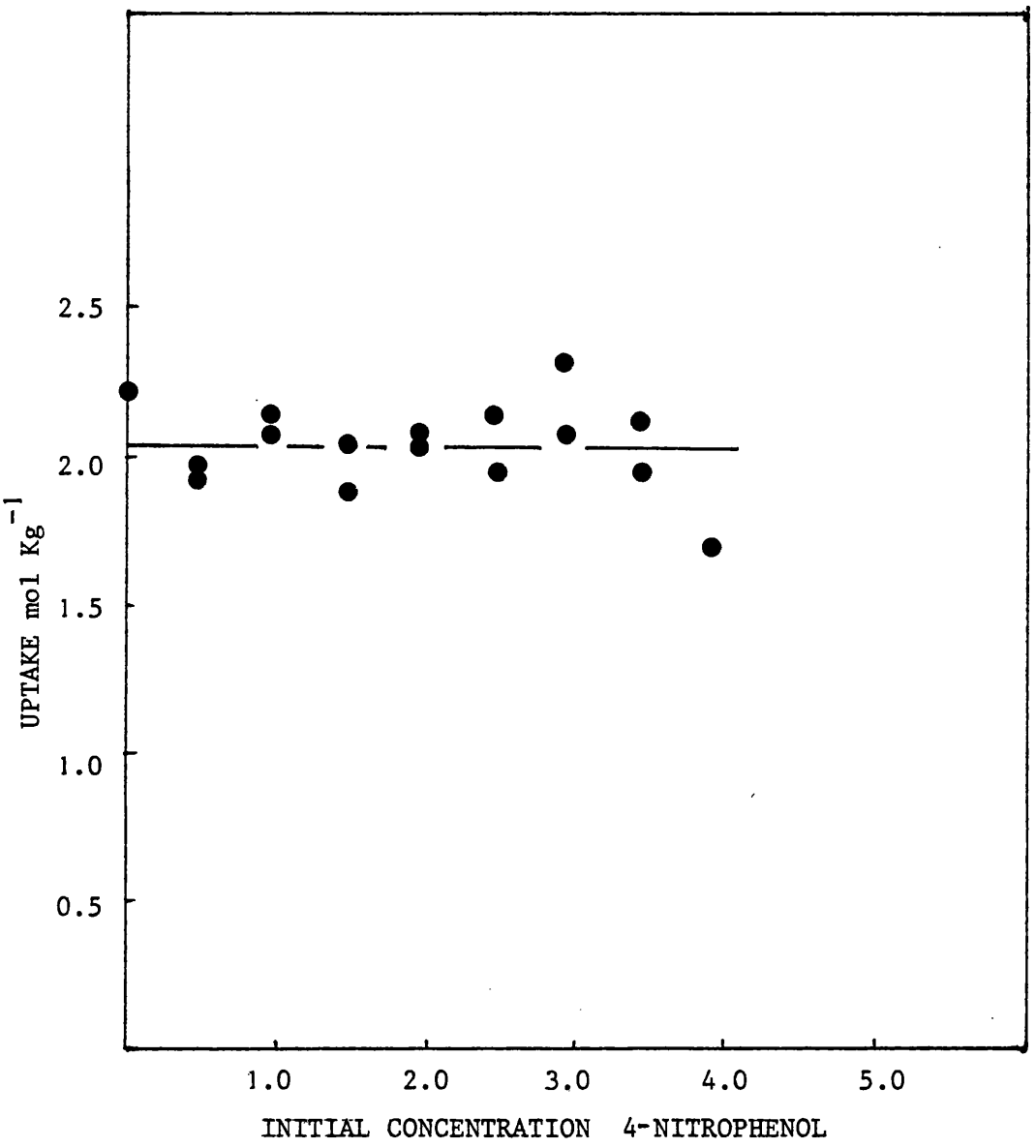


FIG 3.41 MIXED SORPTION SINGLE POINT PLOT FOR ETHYL 4-AMINOBENZOATE BY NYLON 6 COATED ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} IN THE PRESENCE OF 4-NITROPHENOL

INITIAL CONCENTRATION, ETHYL 4- AMINOBENZOATE: 5 x 10^{-3}M

affected by the presence of 4-nitrophenol, however, linear regression analysis suggests that a trend may exist. Table 3.37 shows that the coefficient of variation for the nylon 6 coated sorbent is less than 100% but the correlation is also less than 0.5. As no significant trend is positively established either by visual inspection of figure 3.41 or numerically, competitive sorption was considered not to be taking place. This observation suggests that a difference exists between the pattern of suppresion on the coated and uncoated carbons but is consistent with the result shown in figure 3.37, where suppression of ethyl 4-aminobenzoate uptake by 4-methoxybenzoic acid is abolished after application of the coat (tables 3.36 and 3.37).

3.4. KINETIC STUDIES OF THE SORPTION OF MODEL SOLUTES BY UNCOATED AND NYLON 6 COATED ACTIVE CARBON.

3.4.1 General Method for the Determination of Kinetic Profiles.

The method used in the determination of the rate of sorption was that described by Weber and Morris (1963). A glass conical flask of a nominal value of 1 litre was immersed in a thermostatted water bath at 30^{o} to a depth level with the neck of the flask. To this, 1 litre of test solution was added after a spectrophotometric assay had been carried out to confirm that the initial concentration of the solutes was that required. The solution was discarded if the value for the initial concentration obtained from the spectrophotometric assay differed from that predicted from the dissolution of an accurately weighed sample of solute into buffer at pH 2.32 (0.5 ionic strength). The solution was allowed to equilibrate to the required temperature of 30^{o} before commencement of the experimental determination. The solution was stirred by a glass stirrershaft, fitted with a P.T.F.E.

paddle which was driven by high speed electric motor controlled by a Variac transformer. The shaft speed was accurately determined at 5 minute intervals during the experiment using a xenon strobescope which had been calibrated with a tachometer. An accurately weighed sample of sorbent granules was rapidly added and 4 ml aliquots of the supernatant removed at various time intervals using sintered glass sampling tubes. In order to minimise errors in uptake of the sorbate due to the removal of solution, the kinetic profiles were obtained from three replicate determinations. The kinetic profile was determined over a period of 300 minutes which was subdivided into three time intervals of 0 - 25, 0 - 100 and 0 - 300 minutes, removing five 4 ml samples in each interval so that the total volume removed during any one determination did not exceed 2% of the total volume. These samples were assayed spectrophotometrically to obtain values for the uptake from the mass balance equation (equation 1.1).

Treatment of Results.

The general method outlined in the previous section gives rise to a plot of uptake versus time which will be referred to as the "kinetic profile". The rate of sorption is the gradient of the kinetic profile which changes as a function of time, as can be seen in figure 3.44. Figure 3.42 shows that sorption is slower at 700 rpm than at the other three higher shaft speeds. Table 3.38 further suggests that the relative rate constant at 800 rpm may be significantly slower, however, there appears to be no significant difference at shaft speeds of 900 and 1000 rpm. Two replicate determinations of the relative rate constant at 900 and 1000 rpm shaft speed were compared by means of an F-test where no significant difference was apparent at the 95% level

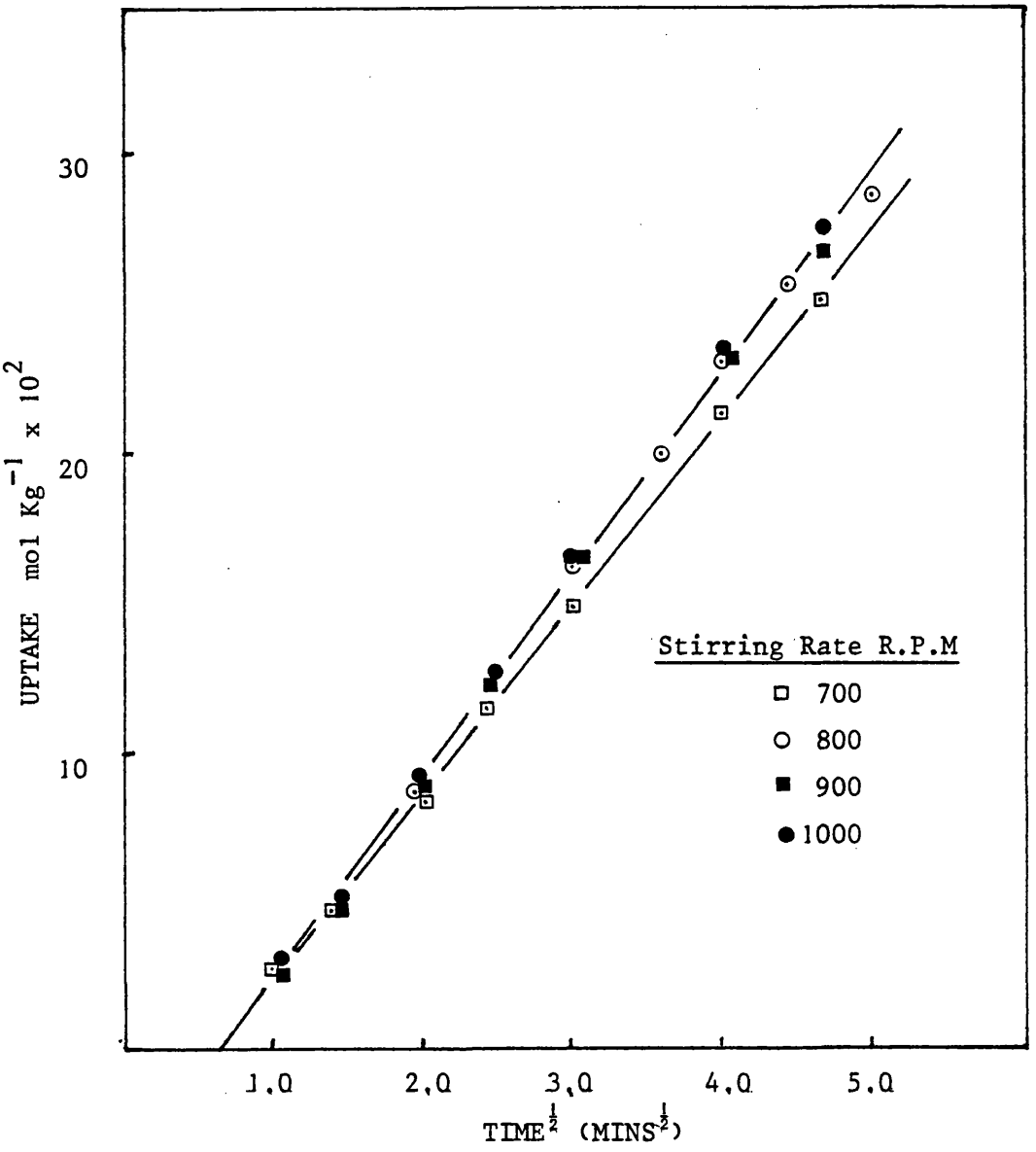


FIG 3.42. EFFECT OF STIRRING RATE ON THE KINETIC PROFILE FOR THE ADSORPTION OF 4-NITROPHENOL (INITIAL CONCENTRATION 10^{-3}M) ON TO 2.0 GRAMME OF ACTIVE CARBON AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° FROM 1000 ml OF SOLUTION.

of significance. A stirring rate of 1000 rpm was therefore used throughout to determine the kinetic profiles of the solutes.

The linear nature of the $t^{\frac{1}{2}}$ plot allows the comparison of relative initial rates of sorption by means of their slopes which have been used to define a "relative rate constant" (Weber and Morris 1963). This relative sorption rate constant does not have the usual dimensions associated with reaction rate constants, being expressed in units of mol $Kg^{-1}t^{-\frac{1}{2}}$.

3.4.2 Preliminary Kinetic Investigations.

3.4.2.1 The Influence of Stirring Rate on the Rate of Sorption.

The rate of sorption of solutes by active carbon has been shown to be dependent on stirring rate (Weber and Morris 1963). The rate of sorption increases with stirring rate up to a critical value after which no further effect is observed. The influence of stirring rate on sorption was determined using a 10^{-3} M 4-nitrophenol solution in contact with 2.0 gramme of active carbon granules over a limited time period of 25 minutes. Stirrer speeds studied were 700, 800, 900 and 1000 rpm. The data, shown in figure 3.42, using the $t^{\frac{1}{2}}$ plot, indicates that they are linear over the initial 25 minute period after an initial lag time of about half a minute. Table 3.38 shows the data obtained from computerised least-squares regression analysis to obtain the relative rate constants.

3.4.2.2. The Influence of Particle Breakdown on the Rate of Sorption.

Under the conditions of high agitation, at a stirring rate of 1000 rpm the active carbon granules were observed to shed fine particles into the supernatant solution. There were insufficient fine particles to recover and subsequently use for equilibrium and kinetic sorption studies to assess their influence on the overall

Table 3.38 Results of Linear Regression Analysis of Data for the effect of Stirring Rate on the Adsorption Kinetics of 4-nitrophenol on to Active Carbon.

Determination	Stirer Shaft Speed (RPM)	Relative Rate $mol\ Kg^{-1}\ min^{-0.5}\ x10^{2}$	Standard Deviation ^{2} of slope x10	Intercept $mol\ Kg^{-1}\ x10^{2}$	Standard Deviation of Intercept^{2} x 10	Correlation Coefficient
I	700	6.17	0.18	-3.65	0.53	0.997
II	800	6.25	0.19	-2.61	0.97	0.996
III	900	6.94	0.18	-4.23	0.53	0.998
IV	900	6.75	0.19	-4.82	0.78	0.996
V	1000	6.69	0.18	-4.12	0.53	0.996
VI	1000	6.65	0.21	-4.44	0.62	0.996

F test of determinations III - VI - $F_{calc} = 3.04$ $F_{tab\ (P=0.05)3,20} = 3.10$

rate of sorption. It was decided, therefore, to assess the influence of the loss of fine particles on the granules using the following procedure. 5 grammes of active carbon granules were stirred at 1000 rpm in 500ml of distilled water at 30^{o} for five hours. The fine particles shed during this process were then separated by washing the granule slurry, supported on a number 10 mesh sieve, with tap water followed by distilled water then drying to constant weight in a vacuum oven. The kinetic profile of 4-nitrophenol from a 10^{-3} M solution was then determined on normal active carbon granules and granules treated by the process described above, using the standard procedure. A stirrer shaft speed of 600 rpm was used to minimise further attrition of the granules. Data from these determinations are given in table 3.39 and figure 3.43. The t-test between the linear region of the two $t^{\frac{1}{2}}$ plots confirms that no significant difference exists between kinetic profiles the attrited and unattrited carbon. The fine particles shed into the flask during the uptake rate determination, therefore, do not affect the characteristics of the kinetic profile.

3.4.3 The Sorption Kinetics of 4-nitrophenol on to Active Carbon.

3.4.3.1 Precision of the Standard Experimental Method.

This was elucidated by determining the sorption of 4-nitrophenol from a 10^{-3} M solution by 2.0 gramme of active carbon over 0-300 minutes. The data is given in table 3.40 and is shown plotted as a kinetic profile (uptake versus time) in figure 3.44.

The sorption of 4-nitrophenol is rapid over the first 30 minutes followed by a transitional period between 30 and 90 minutes, after which the rate of sorption remains slow, as equilibrium is approached.

Table 3.39 The Effect of Particle Breakdown on the Adsorption Kinetics of 4-nitrophenol on to 2.0 gramme of Active Carbon from 1000ml of Solution at pH2.32 (0.5 ionic strength) at 30°.

UNATTRITED CARBON				ATTRITED CARBON			
time	$time^{\frac{1}{2}}$	concentration x 10^{5} M	uptake x 10^{2} M Kg^{-1}	time	$time^{\frac{1}{2}}$	concentration x 10^{5}M	uptake x 10^{2} M Kg^{-1}
5	2.2	14.03	1.75	5	2.2	13.93	1.72
12	3.5	10.71	3.41	13	3.6	10.64	3.37
21	4.6	7.76	4.88	17	4.1	8.88	4.25
31	5.6	5.97	5.79	19	4.4	8.64	4.37
50	7.1	3.74	6.89	31	5.6	6.03	5.73
78	8.8	2.49	7.51	50	7.1	3.88	6.74
90	9.5	2.23	7.65	75	8.7	2.72	7.33
				99	10.0	2.21	7.58
Initial Concentration : 1.754×10^{-4} M Weight Sorbent 2.003g				Initial Concentration : 1.754×10^{-4} M Weight Sorbent 2.001g.			
LINEAR REGRESSION ANALYSIS*							
Slope		$1.21 \times 10_{-2}$ M $Kg_{-1} min_{-\frac{1}{2}}$		$1.19 \times 10_{-2}$ M $Kg_{-1} min_{-\frac{1}{2}}$			
Standard Deviation		$0.06 \times 10_{-2}$ M $Kg_{-1} min$		$0.06 \times 10_{-2}$ M $Kg_{-1} min$			
Intercept		$-0.84 \times 10_{-2}$ M Kg_{-1}		$-0.84 \times 10_{-2}$ M Kg_{-1}			
Standard Deviation		0.26×10 M Kg		0.24×10 M Kg			
Correlation Coefficient		0.997		0.996			
		4.		5			
t test t_{calc} = 0.24			$t_{tab\ (P=0.05)}$ =	3.37.			

* Comparison of data in the linear region of the kinetic profile below a value of uptake of 6.0 mol Kg^{-1}

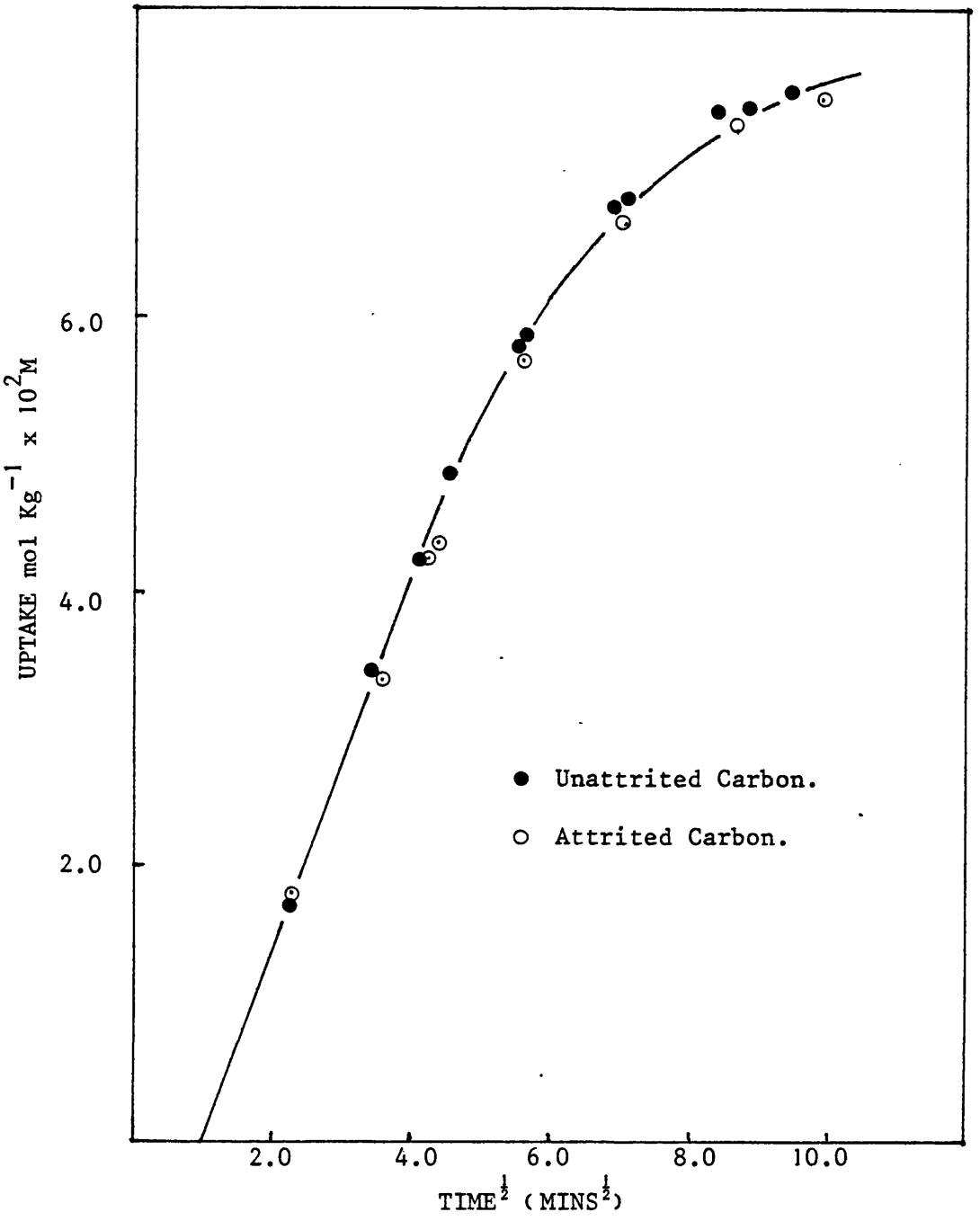


FIG 3.43 THE EFFECT OF PARTICLE BREAKDOWN ON THE ADSORPTION KINETICS OF 4-NITROPHENOL ON TO 2.0 GRAMME OF ACTIVE CARBON FROM 1000ml OF 1.75 x 10^{-4}M INITIAL CONCENTRATION SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°.

Table 3.40 Data for the Rate of Uptake of 4-nitrophenol on to 2.0gramme Active Carbon from 1000ml of 10^{-3} M Aqueous Solution, pH2.32 (ionic strength 0.5M) at 30^{o}.

Time (minutes)	$Time^{0.5}$ ($minutes^{0.5}$)	Uptake mol Kg^{-1}	Percentage residual Concentration
1	1.0	0.029	94.2
4	2.0	0.095	83.0
9	3.0	0.165	66.8
13	3.6	0.207	58.4
16	4.0	0.233	53.2
20	4.5	0.259	48.0
25	5.0	0.288	42.1
36	6.0	0.337	32.4
60	7.8	0.384	22.1
129	11.4	0.436	11.7
180	13.4	0.449	9.2
240	15.5	0.456	7.8
300	17.3	0.461	6.8
Determination II			
2	1.4	0.048	89.3
3	1.7	0.069	85.2
4	2.0	0.090	81.0
6	2.5	0.121	74.7
9	3.0	0.159	67.0
13	3.6	0.230	52.8
18	4.2	0.243	50.3
22	4.7	0.268	46.3
90	9.5	0.412	17.5
180	13.4	0.452	9.1
300	17.3	0.466	6.7

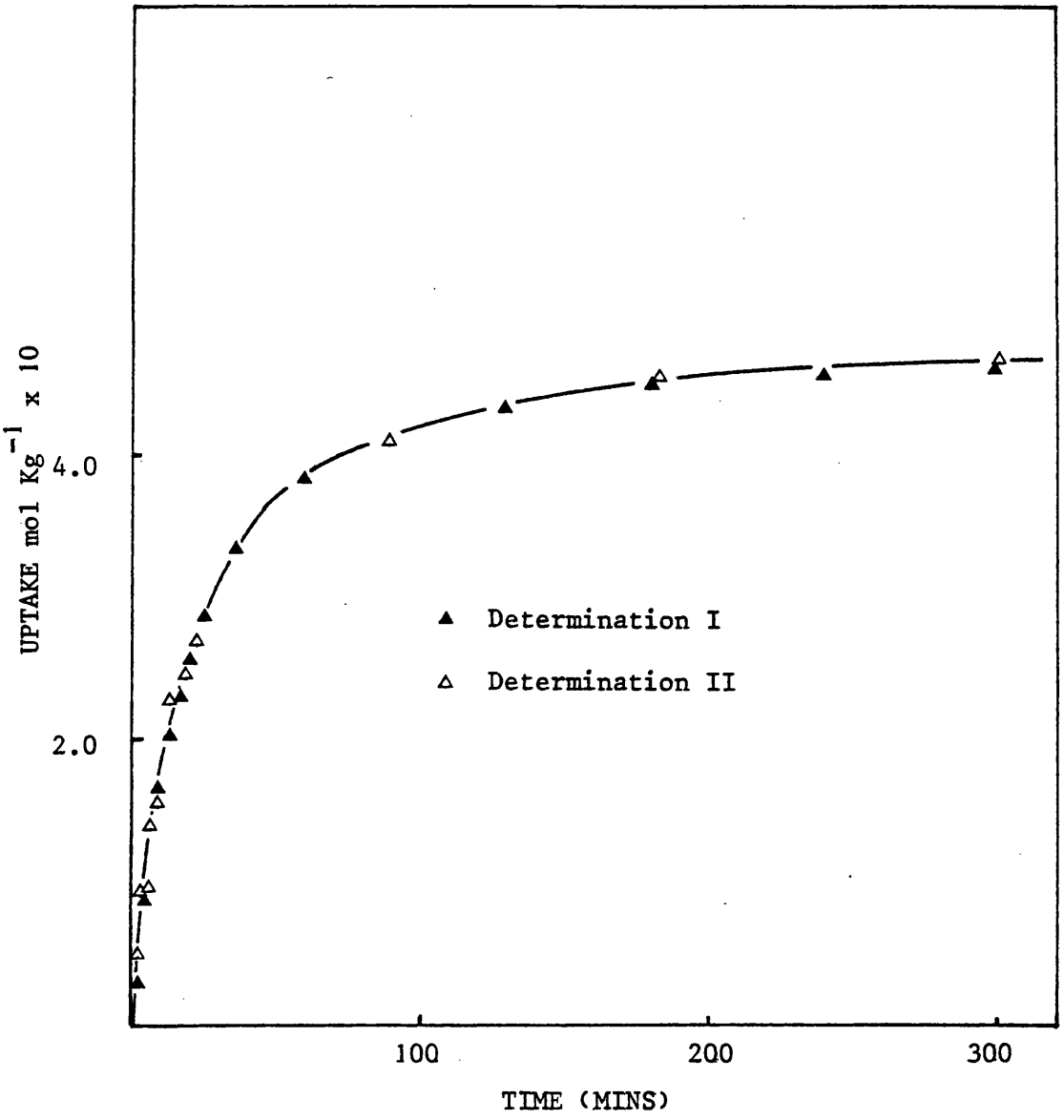


FIG 3.44 DATA FOR THE KINETIC PROFILE OF 4-NITROPHENOL ON TO 2.0 GRAMME OF ACTIVE CARBON FROM 1000ml OF 10^{-3}M SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°

Treatment of Results.

The data is shown plotted as uptake versus $t^{\frac{1}{2}}$ in figure 3.45 where the kinetic profile is linear over the 4-30 minute time period. Data from the linear region of this plot was submitted to a linear least-squares regression analysis to obtain the relative rate constants. These relative rate constants, together with the other parameters associated with the linear profile, are given in table 3.41.

3.4.3.2. The Influence of Active Carbon Weight.

The kinetic profiles of 4-nitrophenol from 1 litre of a 2×10^{-3} M solution were determined using 0.5, 1.0 and 2.0 gramme of active carbon to assess the effect of granule weight on the rate of sorption. The data are plotted as kinetic profiles in figure 3.46 and uptake versus $t^{\frac{1}{2}}$ in figure 3.47. Relative rate constant data is given in table 3.42 where it can be seen that the rate of sorption increases as the weight of sorbent decreases. Although the sorption rate constant increases as the sorbent weight decreases, the total amount of solute removed from solution increases with increasing sorbent weight.

3.4.3.3. The Influence of Initial Concentration.

The kinetics of uptake of 4-nitrophenol from 1 litre of solution of initial concentration $1 - 5 \times 10^{-3}$ M, were determined using 1.0 and 2.0 gramme of active carbon to assess the influence of solute concentration on rates of sorption. Kinetic profiles are shown in figures 3.48 and 3.49 respectively and the corresponding $t^{\frac{1}{2}}$ plots are shown in figure 3.50 and 3.51 respectively. Rate constant data is given in table 3.43 where it can be seen that an increase in initial concentration results in an increased rate of sorption.

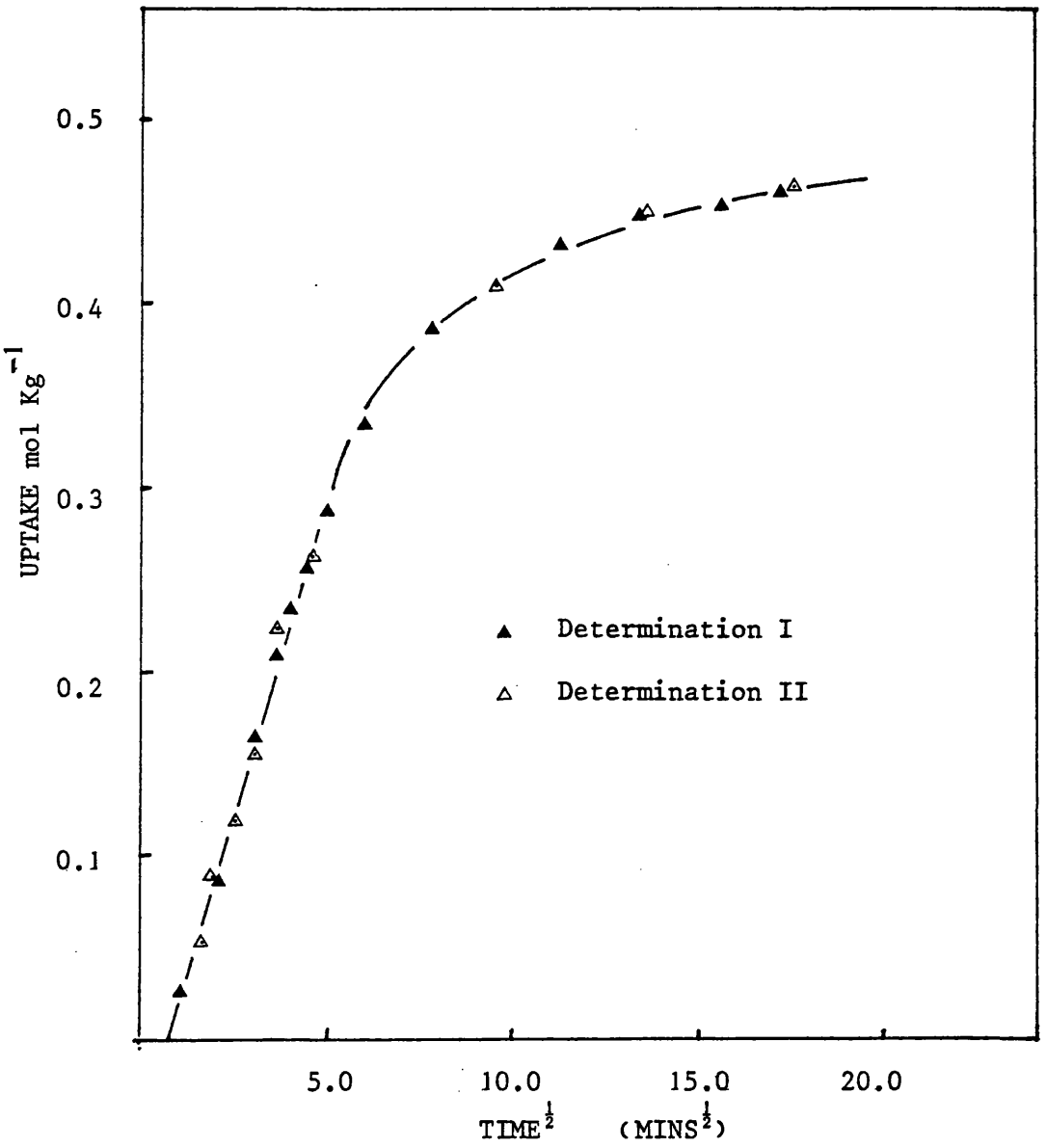


FIG 3.45 DATA FOR THE KINETIC PROFILE OF 4-NITROPHENOL ON TO 2.0 GRAMME OF ACTIVE CARBON FROM 1000ml OF 10^{-3}M INITIAL CONCENTRATION SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} AS A FUNCTION OF SQUARE - ROOT OF TIME

Table 3.41 Data for the Sorption of 4-nitrophenol from 1000ml of a 10^{-3}M Solution, pH2.32 (0.5M ionic strength) and 30^{o} on to 2 gramme of Active Carbon.

Determination	Relative Rate Constant $x10^{3}MKg^{-1}Sec^{0.5}$	Standard Deviation $x\ 10^{3}$	Intercept $x10^{2}\ MKg^{-1}$	Standard Deviation of Intercept $x\ 10^{2}$	Correlation Coefficient
I	1.06	0.04	-3.08	0.88	0.996(n=7)
II	1.07	0.05	-2.99	0.75	0.998(n=8)

t-test for slope : $t_{calc} = 0.06$ $t_{tab\ (P=0.05)} = 2.20$

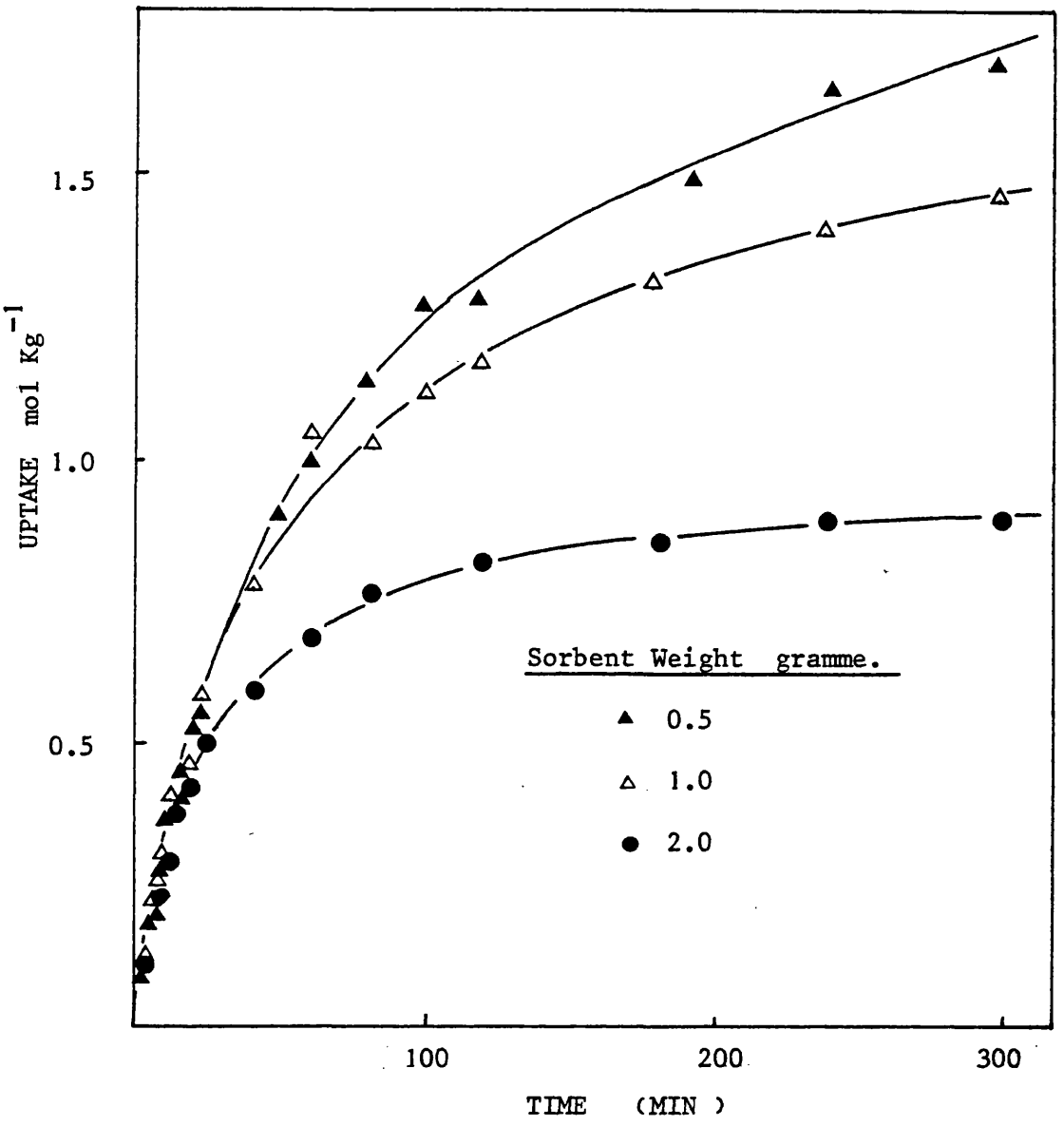


FIG 3.46 THE EFFECT OF ADSORBENT WEIGHT ON THE KINETIC PROFILE OF 4-NITROPHENOL ON TO ACTIVE CARBON FROM 1000ml OF A 2 x 10^{-3}M INITIAL CONCENTRATION SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o}

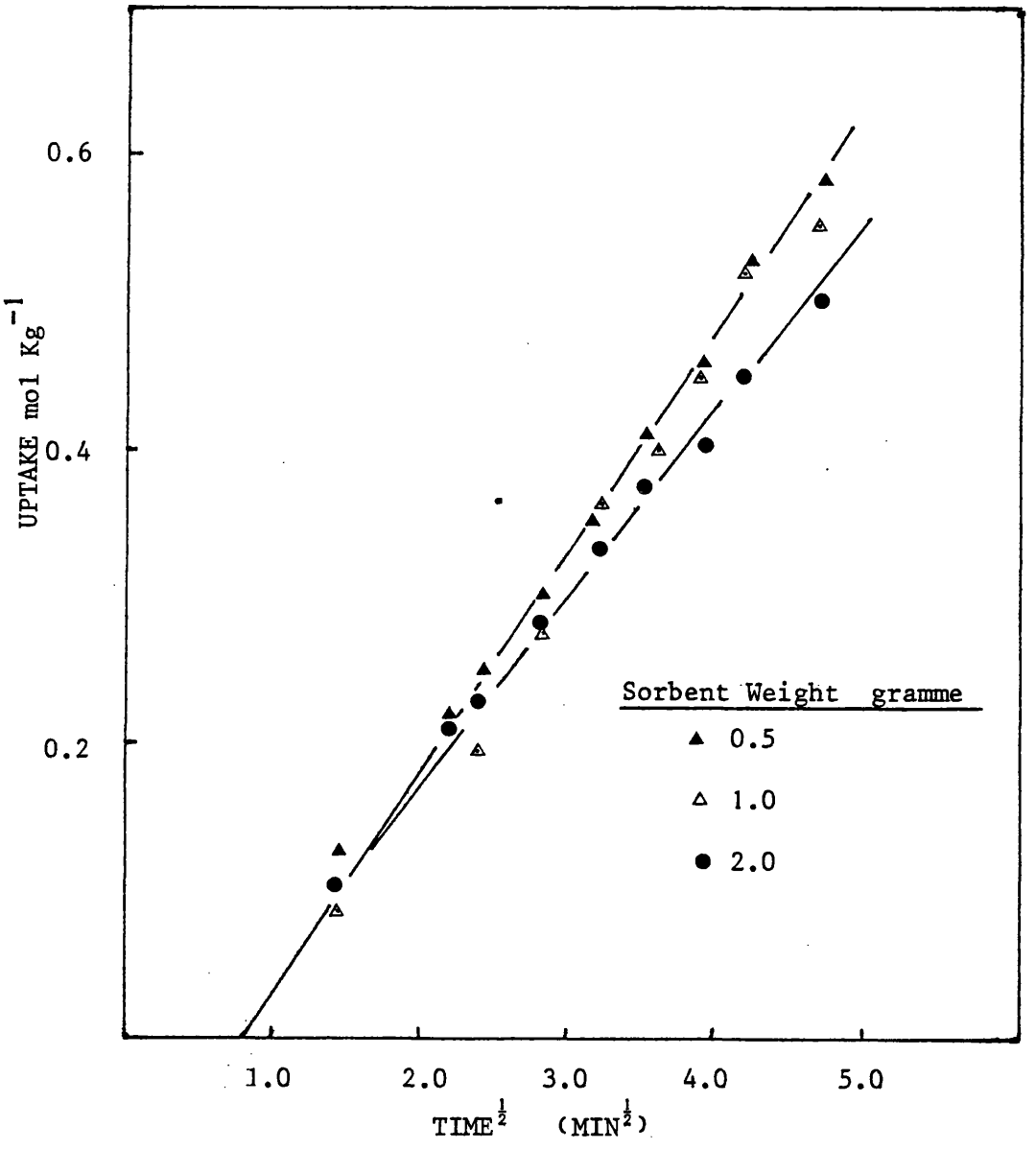


FIG 3.47 THE EFFECT OF GRANULE WEIGHT ON THE KINETIC PROFILE OF 4-NITROPHENOL ON TO ACTIVE CARBON FROM 1000ml OF A 2×10^{-3}M SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° PLOTTED AS A FUNCTION OF THE SQUARE - ROOT OF TIME

Table 3.42 The Influence of Sorbent Weight on the Sorption of 2×10^{-3} M 4-nitrophenol from 1000ml of Solution pH2.32 (0.5M ionic strength), by Active Carbon at 30^{o}.

Sorbent Weight (gramme)	Initial Concentration $\times 10^{3}$ M	Rate Constant $\times 10^{3}$ mol $Kg^{-1} Sec^{0.5}$	Standard Deviation of Rate Constant $\times 10^{3}$	Intercept $\times 10^{2}$ mol Kg^{-1}	Standard Deviation of Intercept	Correlation Coefficient
0.5	1.983	2.47	0.05	-12.70	1.37	0.998
1.0	2.003	2.30	0.05	- 7.30	1.07	0.998
2.0	1.952	2.04	0.03	- 6.35	0.69	0.999

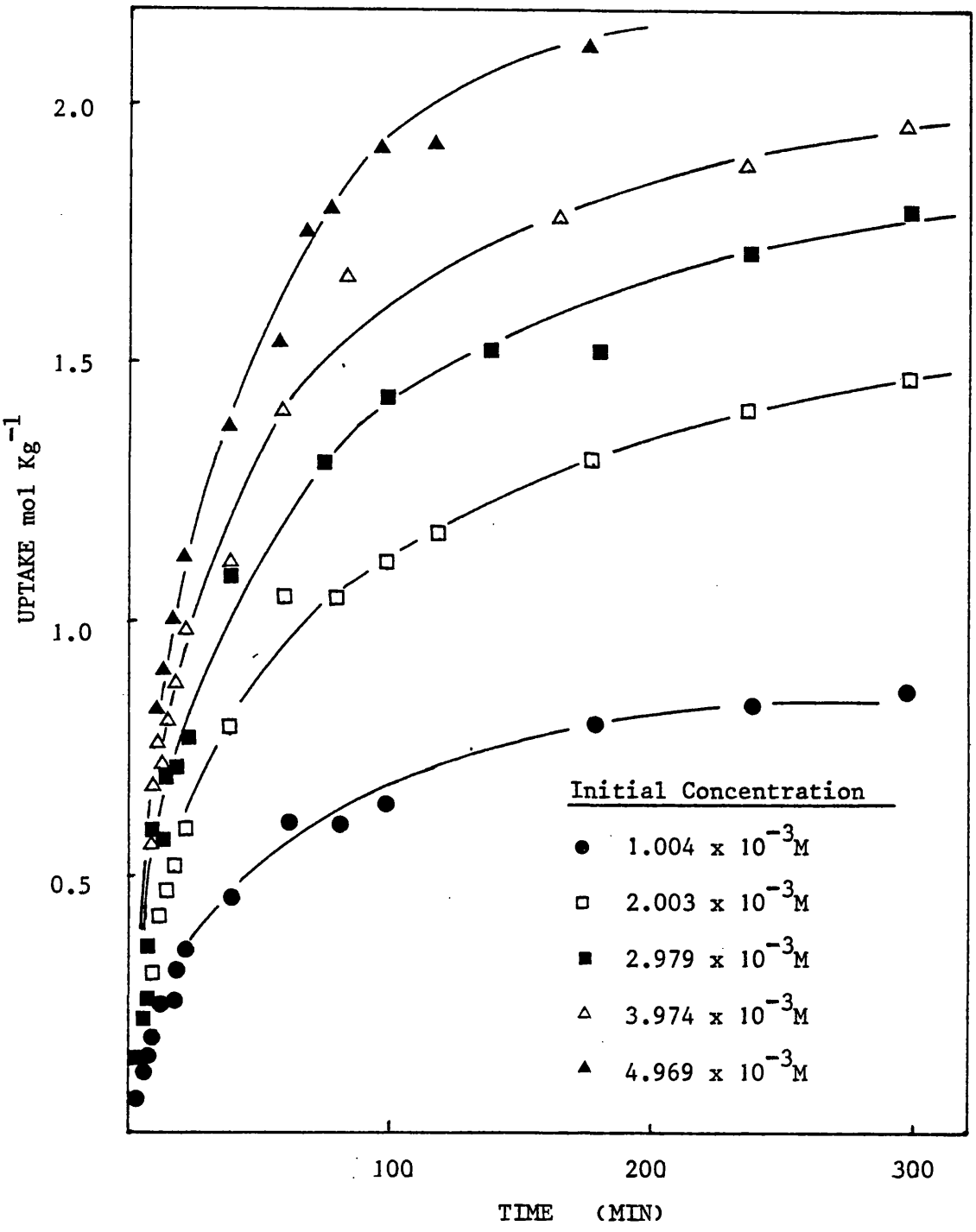


FIG 3.48 THE EFFECT OF INITIAL CONCENTRATION ON THE KINETIC PROFILE OF 4-NITROPHENOL ON TO ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. GRANULE WEIGHT: 1.0 gramme

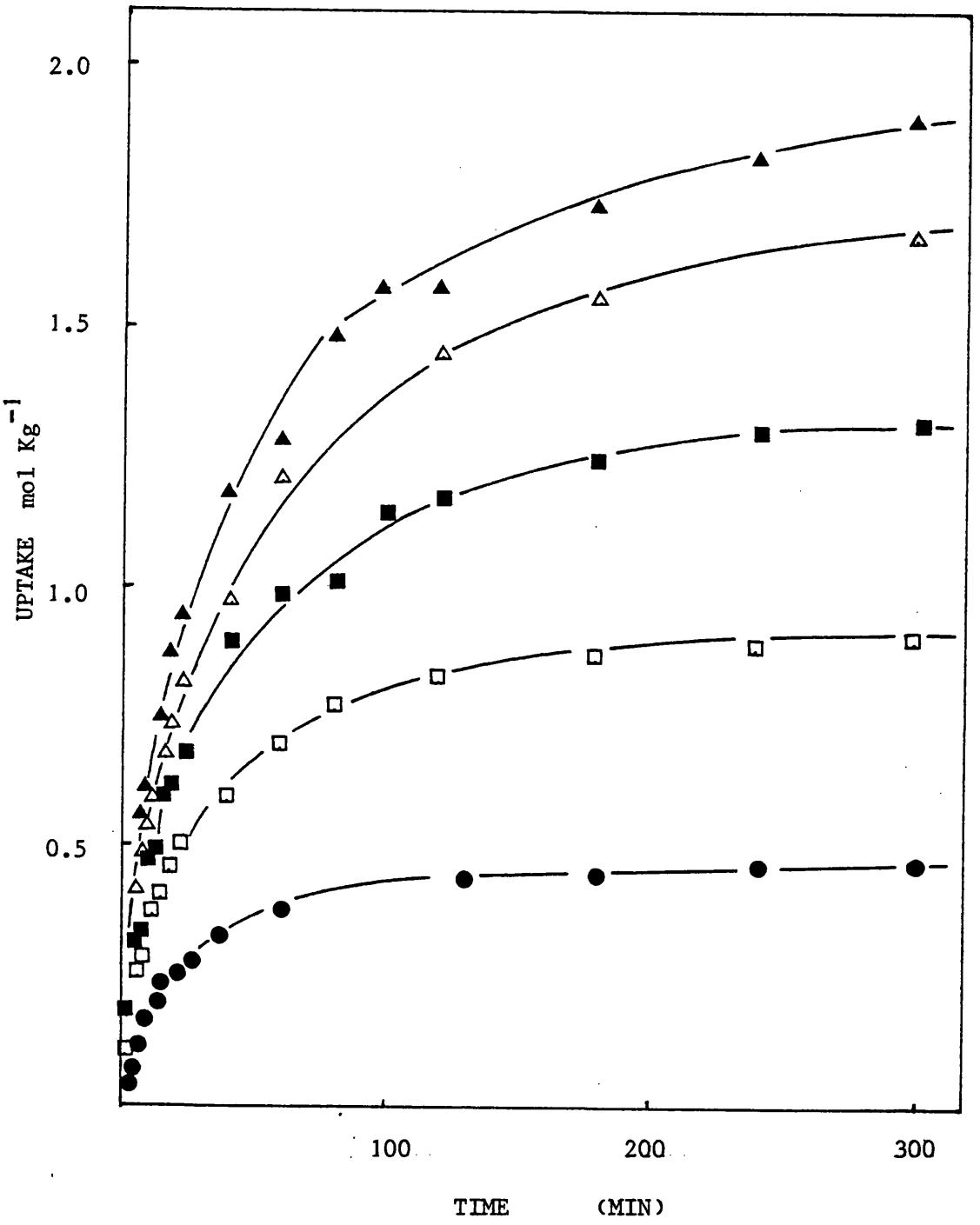


FIG 3.49 THE EFFECT OF INITIAL CONCENTRATION ON THE KINETIC PROFILE OF 4-NITROPHENOL ON TO ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. GRANULE WEIGHT: 2.0 gramme

INITIAL CONCENTRATION: ● 9.990×10^{-4}M; □ 1.952×10^{-3}M; ■ 2.964×10^{-3}M △ 3.961×10^{-3}M; ▲ 4.915×10^{-3}M

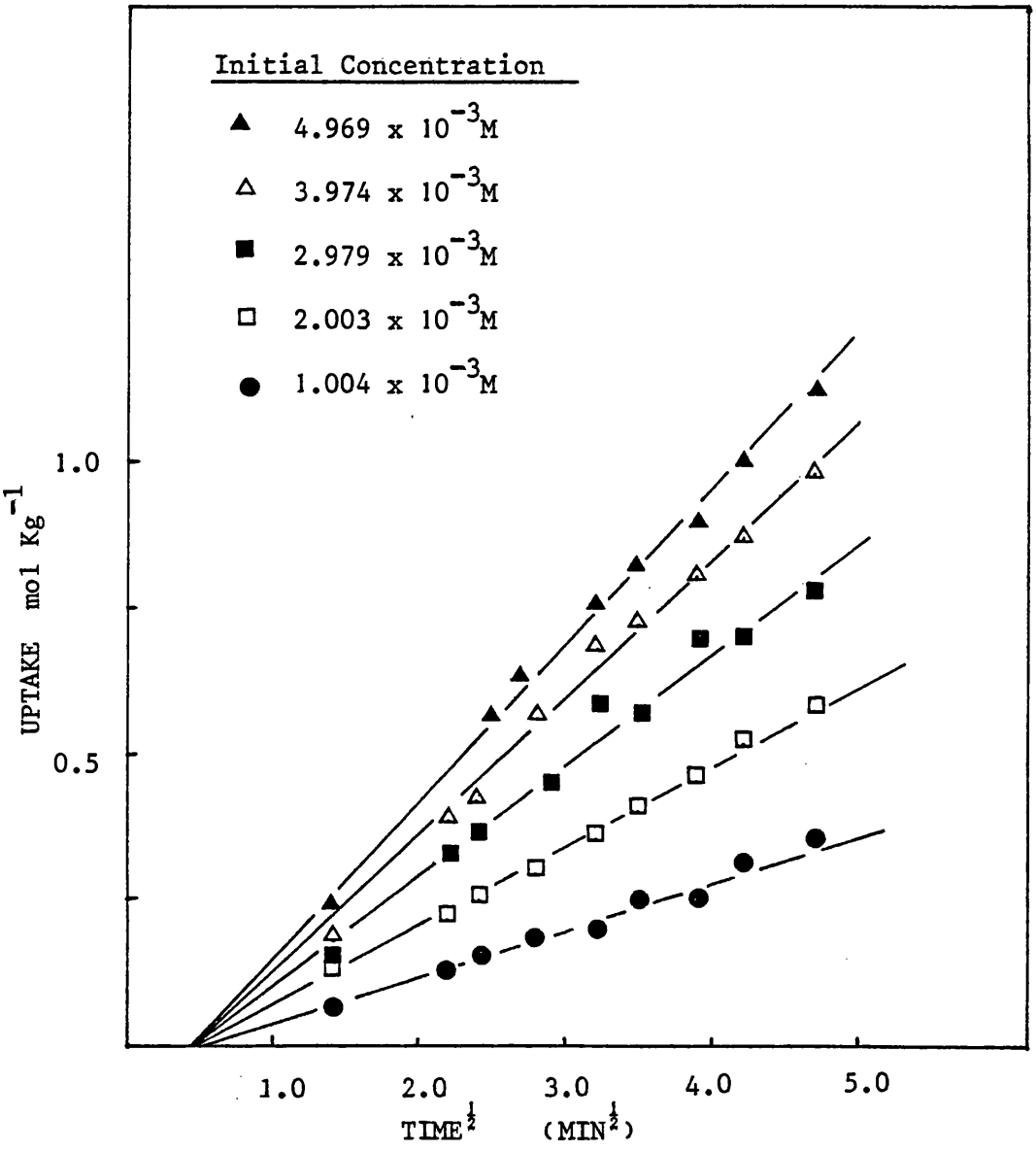


FIG 3.50 THE EFFECT OF INITIAL CONCENTRATION ON THE $t^{\frac{1}{2}}$ PLOTS FOR 4-NITROPHENOL ON TO ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. GRANULE WEIGHT: 1.0 gramme

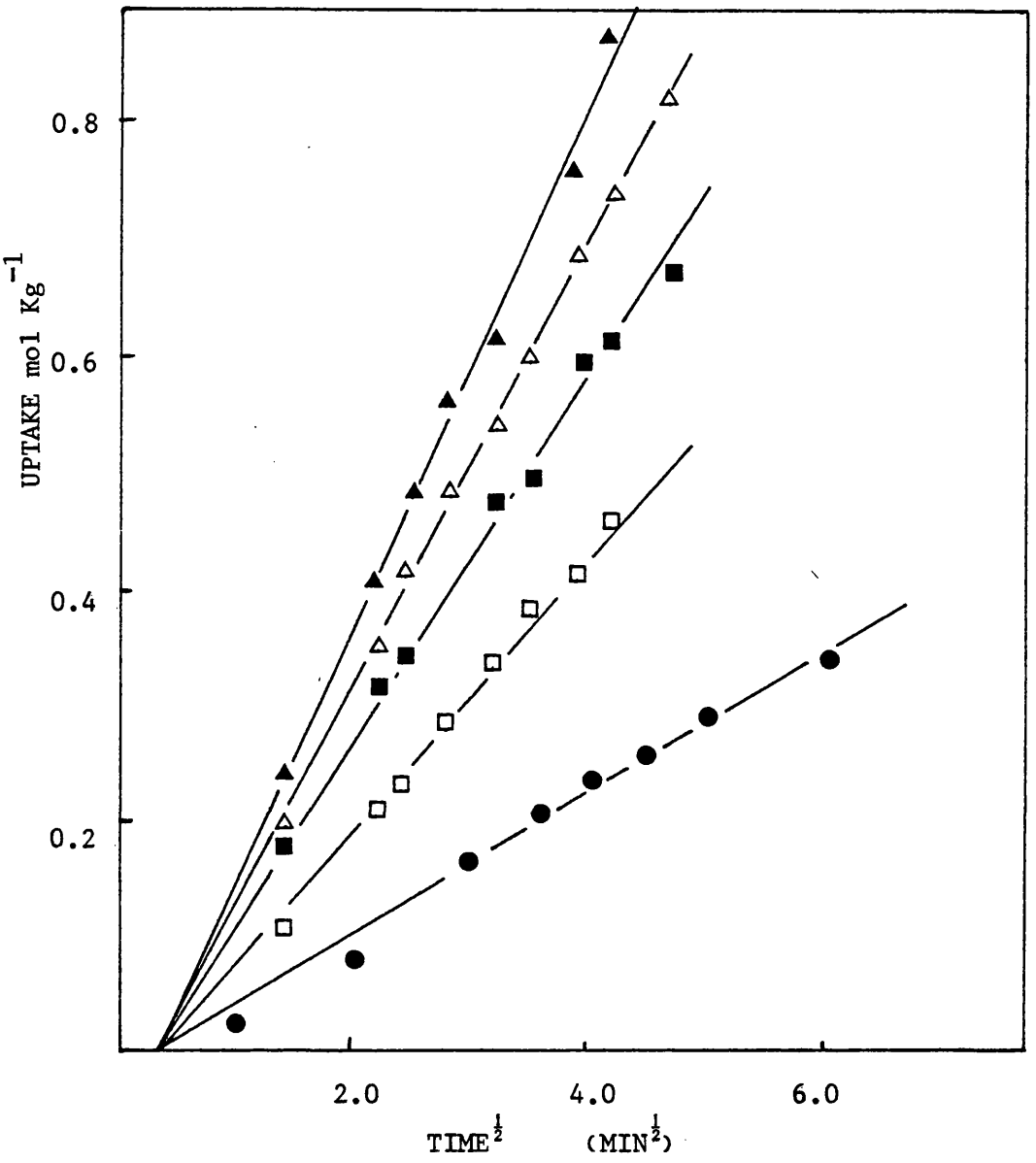


FIG 3.51 THE EFFECT OF INITIAL CONCENTRATION ON THE $t^{\frac{1}{2}}$ PLOTS FOR 4-NITROPHENOL ON TO ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. GRANULE WEIGHT: 2.0 gramme.

INITIAL CONCENTRATION: ▲ 4.915×10^{-3}M; △ 3.961×10^{-3}M; ■ 2.964×10^{-3}M □ 1.952×10^{-3}M; ● 9.990×10^{-4}M.

Table 3.43 The Influence of Initial Solute Concentration on the Rate of Sorption of 4-nitrophenol from 1000ml of Solution (pH2.32, ionic strength 0.5M) at 30° on to Various Weights of Active Carbon.

Initial Concentration $x\ 10^{3}$ M	Adsorbent Weight gramme	Rate Constant $x10^{3}$ mol Kg^{-1} $sec^{0.5}$	Standard Deviation of Rate Constant $x10^{-3}$	Intercept mol Kg^{-1} 10^{2}	Standard Deviation Intercept $x10^{2}$	Correlation Coefficient
1.004	1.0	1.38	0.04	-4.4	1.09	0.995
2.003	1.0	2.30	0.05	-7.3	1.07	0.998
2.979	1.0	3.20	0.08	-9.8	1.54	0.998
3.974	1.0	4.06	0.20	-8.4	3.40	0.995
4.969	1.0	4.32	0.14	-8.6	2.70	0.996
0.999	2.0	1.06	0.04	-3.08	0.88	0.996
1.952	2.0	2.04	0.03	-6.35	0.69	0.999
2.964	2.0	2.74	0.24	-9.02	0.55	0.994
3.961	2.0	3.13	0.06	-5.46	0.12	0.998
4.915	2.0	3.60	0.10	-6.42	0.21	0.997

3.4.3.4. The Influence of Coating Active Carbon Granules with Nylon 6.

The kinetic profile for the sorption of 1 - $5x10^{-3}$ M 4-nitrophenol on to 1.0 gramme of nylon 6 coated active carbon are shown in figure 3.52. The corresponding $t^{\frac{1}{2}}$ plots are shown in figure 3.53 and the relative rate constant data is given in table 3.44.

The relative rate constant for the sorption of 4-nitrophenol generally increases as the initial concentration increases, although the overall sorption rates are lower than for the corresponding profiles on the uncoated sorbent. The rate constants increase from $1x10^{-3}$ M to $3x10^{-3}$ M initial concentration at which point no further increase occurs, for an increase in initial concentration, suggesting that a limiting rate of sorption has been attained.

3.4.4 The Sorption Kinetics of the Model Solute Interaction with Uncoated and Nylon 6 Coated Active Carbon from Single Solute and Binary Solute Solution.

The sorption kinetic profiles of 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate were determined for this interaction with 1.0 gramme of coated and uncoated carbon from 1000ml of solution at pH 2.32 (ionic strength 0.5M) and 30^{o} using the standard procedure. The use of 1.0 gramme of sorbent ensured that uptakes reached values where competition might be expected on the basis of the equilibrium sorption studies. The investigation of the kinetics of sorption in this region of uptake ensured that the effect of competitive sorption processes on the rate of uptake could be studied.

3.4.4.1 The Rate of Sorption of the Model Solutes from Single Solute Solution on Active Carbon.

The sorption kinetics profiles for 4-nitrophenol, 4-methoxybenzoic

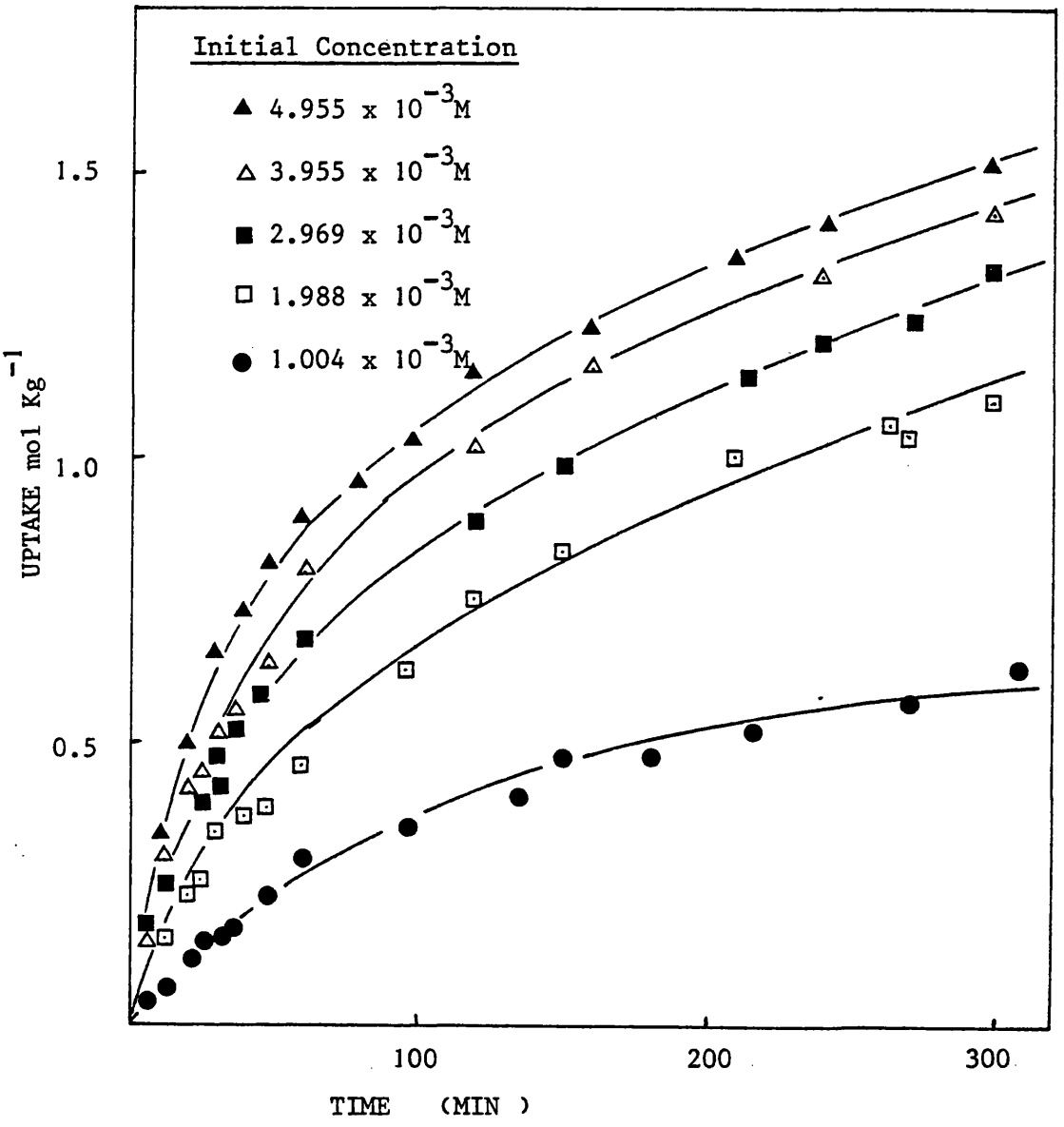


FIG 3.52 THE EFFECT OF INITIAL CONCENTRATION ON THE KINETIC PROFILE OF 4-NITROPHENOL ON TO NYLON 6 ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. GRANULE WEIGHT: 1.0 gramme

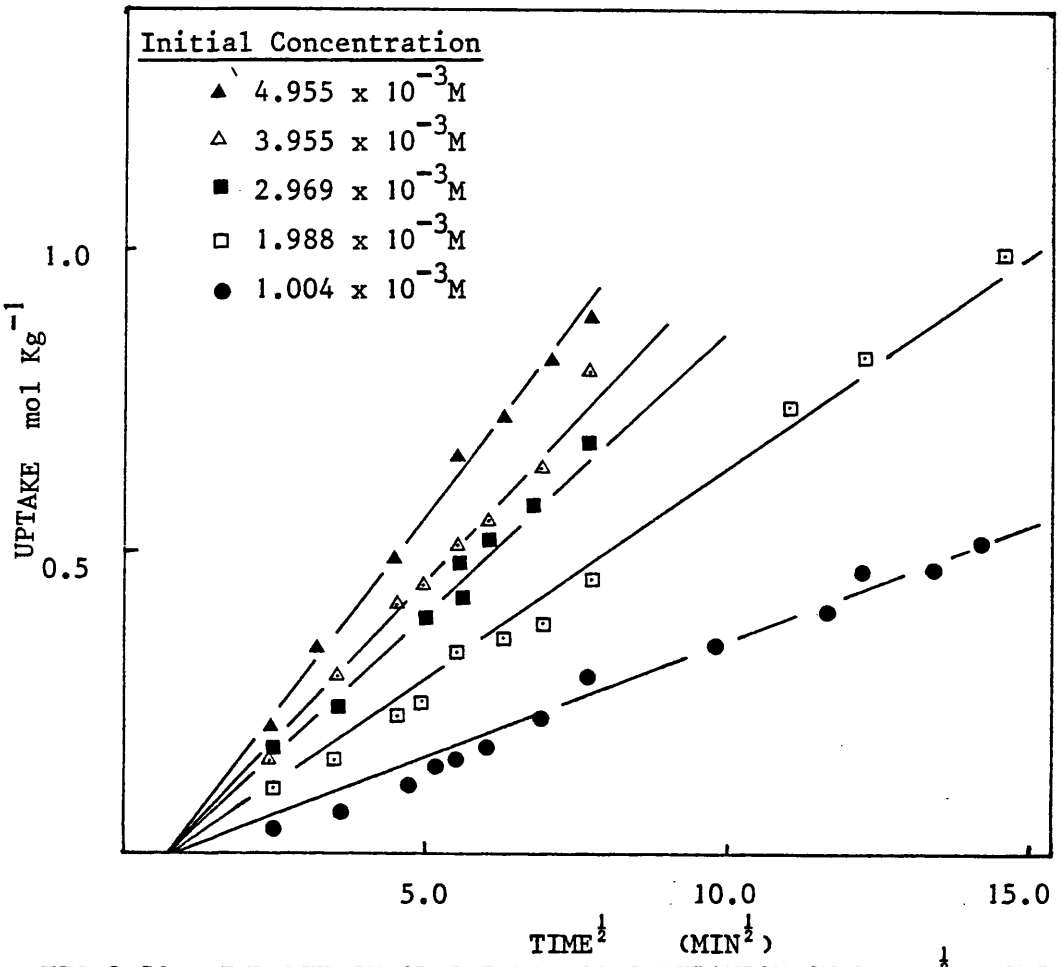


FIG 3.53 THE EFFECT OF INITIAL CONCENTRATION ON THE $t^{\frac{1}{2}}$ PLOTS FOR 4-NITROPHENOL ON TO NYLON 6 COATED ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30°. GRANULE WEIGHT 1.0 gramme.

Table 3.44 The Effect of the Nylon 6 Coat on the Rate of Sorption of 4-nitrophenol from 1000ml of Solution of Various Initial Concentration by 1.0 gramme of Sorbent at pH2.32 (0.5M ionic strength).and 30^{o}.

Initial Concentration $\times 10^{3}$ M	Rate Constant $\times 10^{3}$ mol Kg^{-1} $Sec^{-0.5}$	Standard Deviation of Rate Constant $\times 10^{3}$	Intercept $\times 10^{2}$ mol Kg^{-1}	Standard Deviation of Intercept $\times 10^{2}$	Correlation Coefficient
1.004	0.67	0.02	-5.7	1.22	0.995
1.988	1.17	0.03	-7.1	1.93	0.996
2.969	1.64	0.09	-8.5	3.12	0.990
3.955	1.74	0.09	-7.7	2.94	0.994
4.955	1.87	0.12	-0.6	4.73	0.990

acid and ethyl 4-aminobenzoate from 1 litre of 10^{-3} M solution on active carbon are shown in figure 3.54 and the corresponding $t^{\frac{1}{2}}$ plots are shown in figure 3.55. The $t^{\frac{1}{2}}$ plots were all linear up to 25 minutes allowing relative rate constants to be calculated in each case which are given in table 3.45. The relative rate constants for the sorption of 4-nitrophenol (figure 3.50) and ethyl 4-aminobenzoate (not plotted) from $5x10^{-3}$ M solution are also given in table 3.45 for comparison. These two systems will be used, subsequently, in the binary solute sorption study.

3.4.4.2 The Rate of Sorption of the Model Solutes from Single Solute Solution on Nylon 6 Coated Active Carbon.

The sorption kinetics profiles for 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate from 1 litre of a 10^{-3} M solution on nylon 6 coated active carbon are shown in figure 3.56 and the corresponding $t^{\frac{1}{2}}$ plots in figure 3.57. The $t^{\frac{1}{2}}$ plots were linear up to 3 hours and the relative sorption rate constants are given in table 3.46, also included are data for the sorption of 4-nitrophenol and ethyl 4-aminobenzoate from $5x10^{-3}$ M solutions, which were used in binary solute sorption rate studies. The rank order of the overall rates of sorption is different from that of the uncoated sorbent. For the coated carbon, the sorption rate profiles of 4-nitrophenol and 4-methoxybenzoic acid (figure 3.56) superimpose whilst that for ethyl 4-aminobenzoate remains lower. The overall rate of sorption for all three solutes is lower on the nylon 6 coated carbon compared to the uncoated material.

3.4.5 The Uptake of Solutes from Binary Mixed Solution on to Active Carbon and Nylon 6 Coated Active Carbon.

Kinetic data for sorption from binary mixed solutions of the

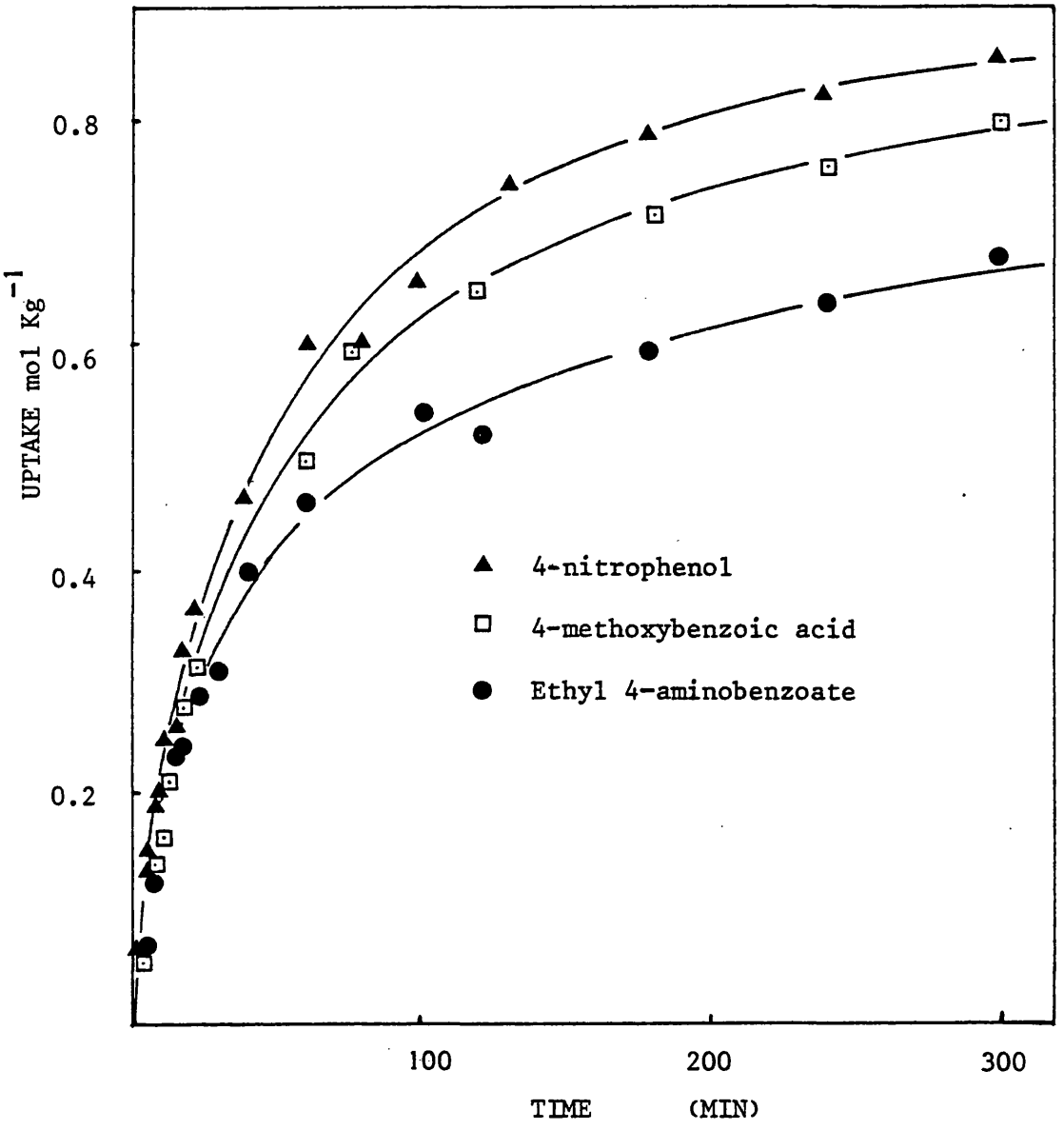


FIG 3.54 THE KINETIC PROFILES FOR 4-NITROPHENOL, 4-METHOXYBENZOIC ACID AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF 10^{-3}M INITIAL CONCENTRATION SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} ON TO 1.0 gramme ACTIVE CARBON.

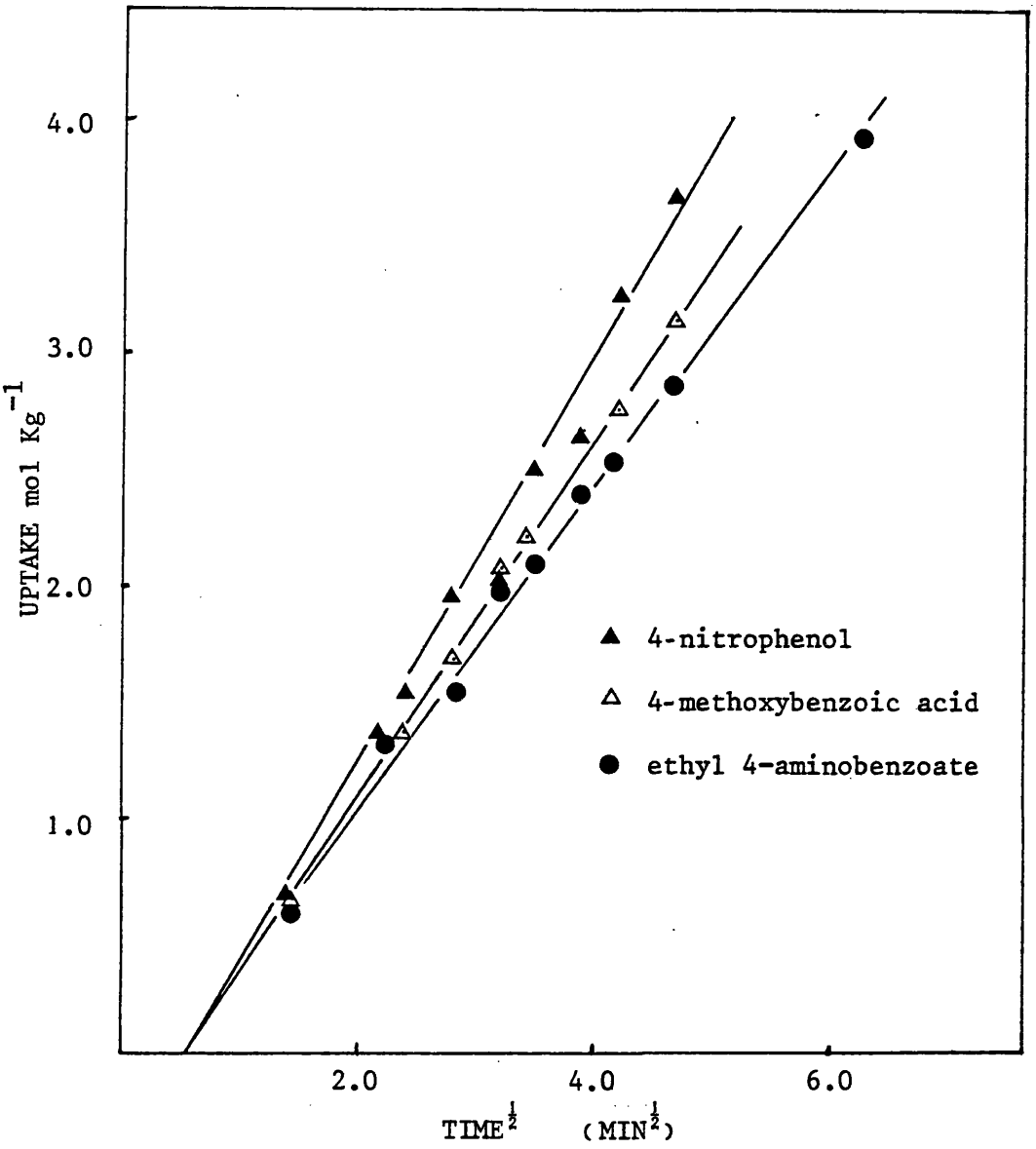


FIG 3.55 $t^{\frac{1}{2}}$ PLOTS FOR THE SORPTION OF 4-NITROPHENOL, 4-METHOXYBENZOIC-ACID AND ETHYL 4-AMINOBENZOATE ON TO ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{O}. INITIAL CONCENTRATION: 10^{-3}M; SORBENT WEIGHT; 1.0 gramme

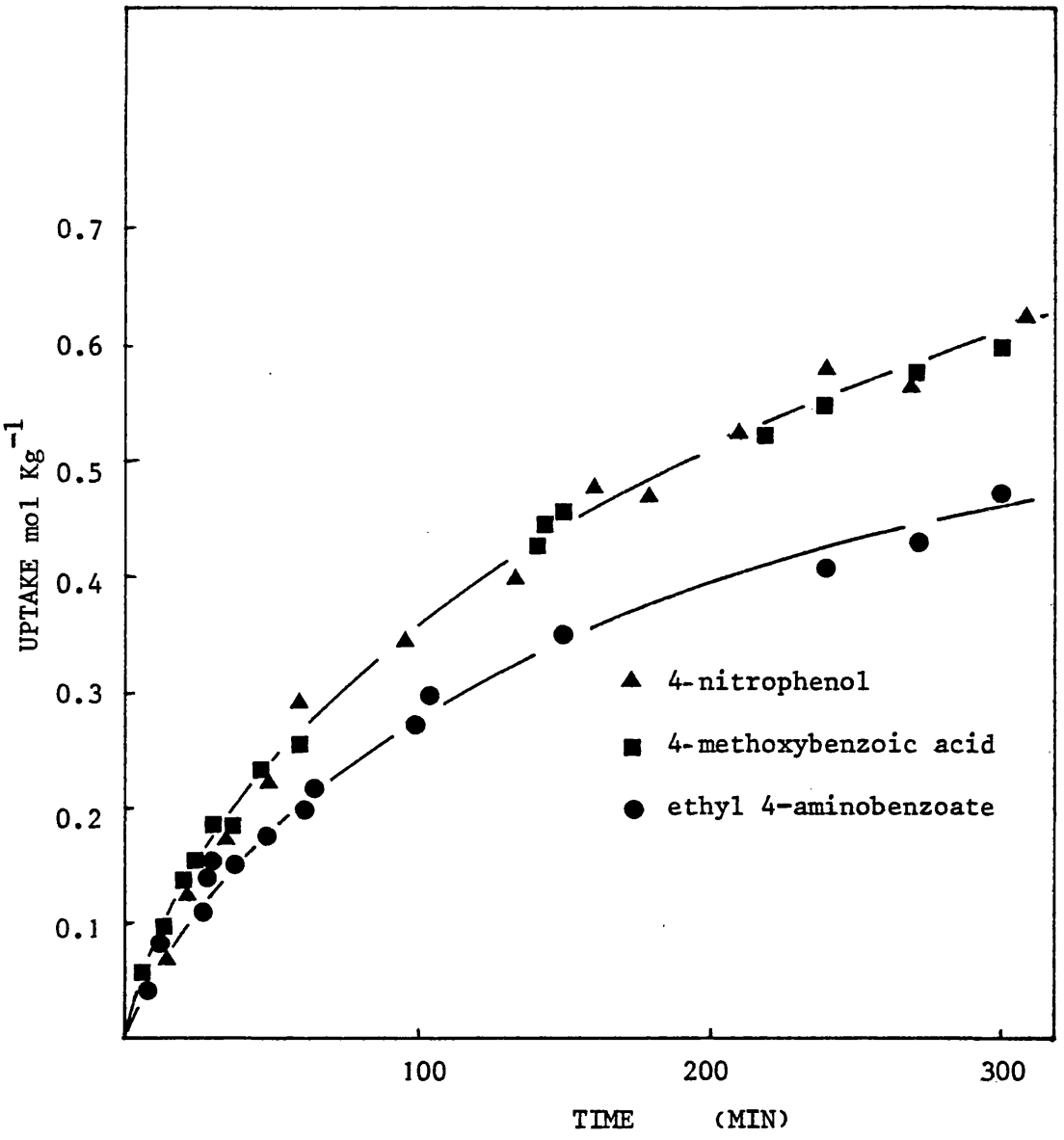


FIG 3.56 KINETIC PROFILES FOR 4-NITROPHENOL, 4-METHOXYBENZOIC ACID AND ETHYL 4-AMINOBENZOATE ON TO NYLON 6 COATED ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} INITIAL CONCENTRATION: 10^{-3}M; SORBENT WEIGHT 1.0 gramme

Table 3.45 Rate Constant Data for the Sorption of 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate from 1000ml of Solution at pH2.32 (0.5M ionic strength) and 30^{o} on to 1.0 gramme of Active Carbon.

Solute	Initial Concentration $x10^{3}$ M	Relative Rate Constant $x10^{3}$ mol Kg^{-1} $Sec^{-0.5}$	Standard Deviation of Rate Constant $x\ 10^{3}$	Intercept $x10^{2}$ mol Kg^{-1}	Standard Deviation of Intercept $x\ 10^{2}$	Correlation Coefficient
4-nitrophenol	1.004	1.38	0.04	-4.4	1.09	0.995
4-methoxybenzoic acid	1.003	1.21	0.06	-3.7	1.55	0.991
ethyl 4-amniobenzoate	0.985	1.04	0.03	-1.5	8.91	0.995
4-nitrophenol	4.969	4.32	0.14	-8.6	2.70	0.996
ethyl 4-aminobenzoate	4.925	2.72	0.03	-7.2	5.06	0.997

The rank order of overall rate of uptake is as follows:

4-nitrophenol > 4-methoxybenzoic acid > ethyl 4-aminobenzoate

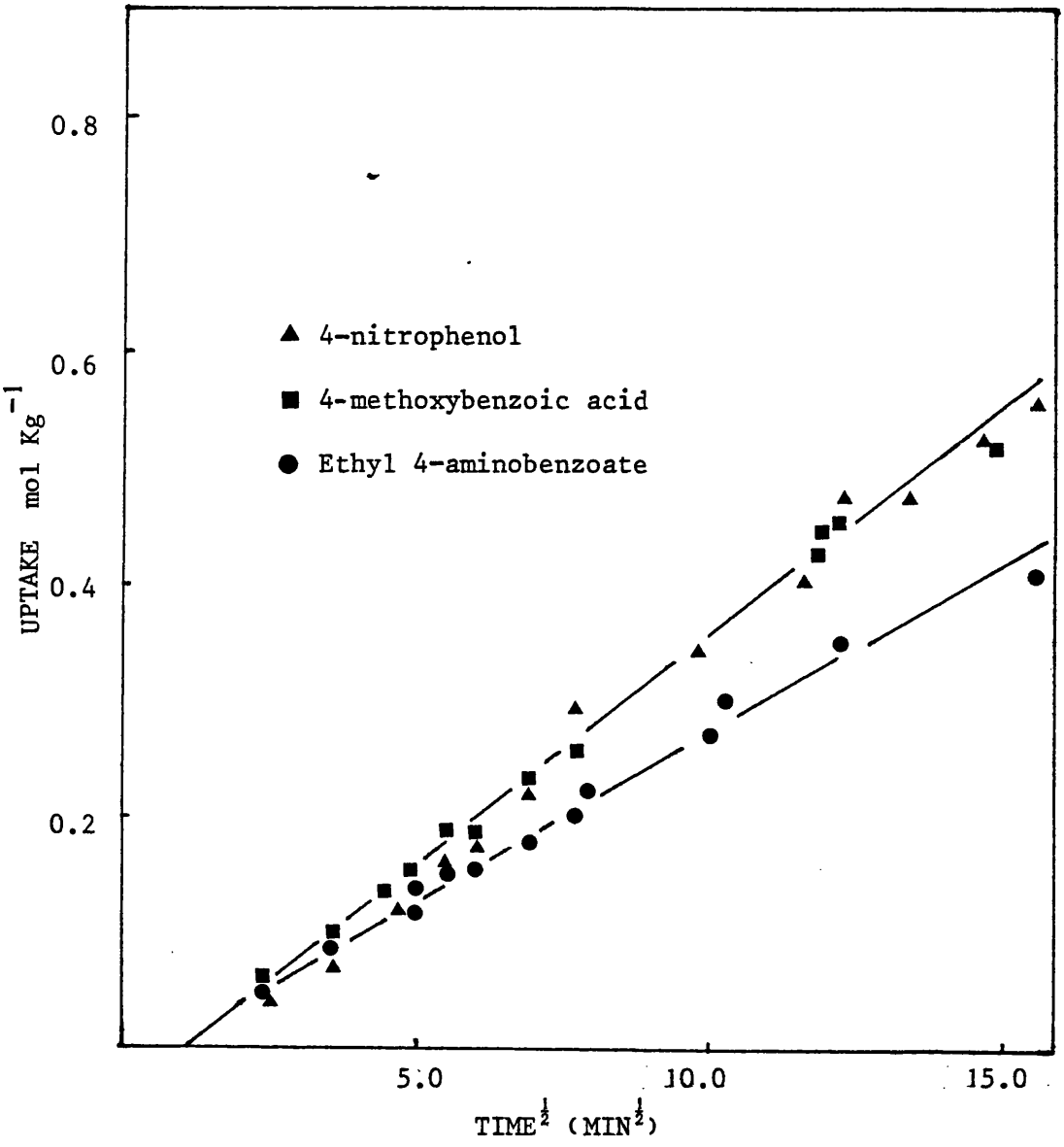


FIG 3.57 $t^{\frac{1}{2}}$ PLOTS FOR 4-NITROPHENOL, 4-METHOXYBENZOIC ACID AND ETHYL 4-AMINOBENZOATE ON TO NYLON 6 COATED ACTIVE CARBON FROM 1000ml OF SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° INITIAL CONCENTRATION: 10^{-3}M; GRANULE WEIGHT 1.0 gramme

Table 3.46 Relative Adsorption Rate Constant Data for the Uptake of 4-nitrophenol 4-methoxybenzoic acid and ethyl 4-aminobenzoate by 1.0 gramme of Uncoated Nylon 6 Coated Active Carbon from 1000ml of Solution at pH2.32 (ionic strength 0.5M) at 30°.

Adsorbate	Initial Concentration $x10^{3}$ M	Rate Constant $x10^{3}$ mol Kg^{-1} $Sec^{-0.5}$	Standard Error of Rate Constant $x10^{3}$	Intercept $x10^{2}$ mol Kg^{-1}	Standard Error of Intercept $x10^{2}$	Correlation Coefficent
Uncoated Active Carbon						
4-nitrophenol	1.004	1.38	0.04	-4.4	1.09	0.995
4-methoxybenzoic acid	1.003	1.21	0.06	-3.7	1.55	0.991
ethyl 4-aminobenzoate	0.985	1.04	0.03	-1.5	8.91	0.995
4-nitrophenol	4.969	4.32	0.14	-8.6	2.70	0.996
ethyl 4-aminobenzoate	4.925	2.72	0.03	-7.2	5.06	0.997
Nylon 6 Coated Active Carbon						
4-nitrophenol	1.004	0.67	0.02	-5.7	1.22	0.995
4-methoxybenzoic acid	1.007	0.65	0.02	-3.8	0.90	0.997
ehtyl 4-aminobenzoate	0.985	0.52	0.02	-2.6	0.77	0.994
4-nitrophenol	4.955	1.87	0.12	0.6	4.73	0.990
ethyl 4-aminobenzoate	4.974	1.00	0.03	-0.1	1.73	0.994

model solutes by both active carbon and nylon 6 coated active carbon were determined at pH 2.32 (0.5M ionic strength) and 30° using the standard procedure. The binary solute mixtures selected for study together with the initial concentration are summarised in table 3.47.

Calculation of relative rate constants from binary solute sorption experiments was not carried out as the nature of the $t^{\frac{1}{2}}$ plots were linear, usually over the initial 25 minute period, but intercept the abscissa with a positive value. Clearly, in systems where the effect of competition is not significant over the initial 0 - 25 minute time interval, the $t^{\frac{1}{2}}$ relationship is followed. When competition is present the $t^{\frac{1}{2}}$ plot is linear but intercepts the ordinate as is shown in figure 3.58. As the validity of the $t^{\frac{1}{2}}$ is questionable for the comparison of single and binary solute sorption kinetics in the presence and absence of the nylon 6 coat, the kinetic profiles only are presented to allow direct comparison of the effect of competitive sorption on the rate of uptake and the effect of the coat on such processes. In all cases, the rate of uptake of solutes was lower on the coated sorbent than on the uncoated material.

3.4.5.1 The Rate of Sorption of Ethyl 4-aminobenzoate and 4-nitrophenol.

Figure 3.59 shows that the kinetic profile for ethyl 4 - aminobenzoate from an initial concentration of 5×10^{-3} M on uncoated active carbon is unaffected by the presence of 4-nitrophenol at an initial concentration of 10^{-3} M. In contrast, the profile for 4-nitrophenol shows that the rate of uptake is reduced by the presence of ethyl 4-aminobenzoate from zero time. The kinetic profiles for

Table 3.47 Binary Mixed Solute Systems used in the Kinetics Studies

Model Solutes		Initial Concentration x 10^3 M		Figure Numbers
1	2	1	2	
ethyl 4-aminobenzoate	4-nitrophenol	5	1	3.58,3.59
4-nitrophenol	ethyl 4-aminobenzoate	5	1	3.60,3.61
ethyl 4-aminobenzoate	4-methoxybenzoic acid	5	1	3.62,3.63
4-nitrophenol	4-methoxybenzoic acid	5	1	3.64,3.65

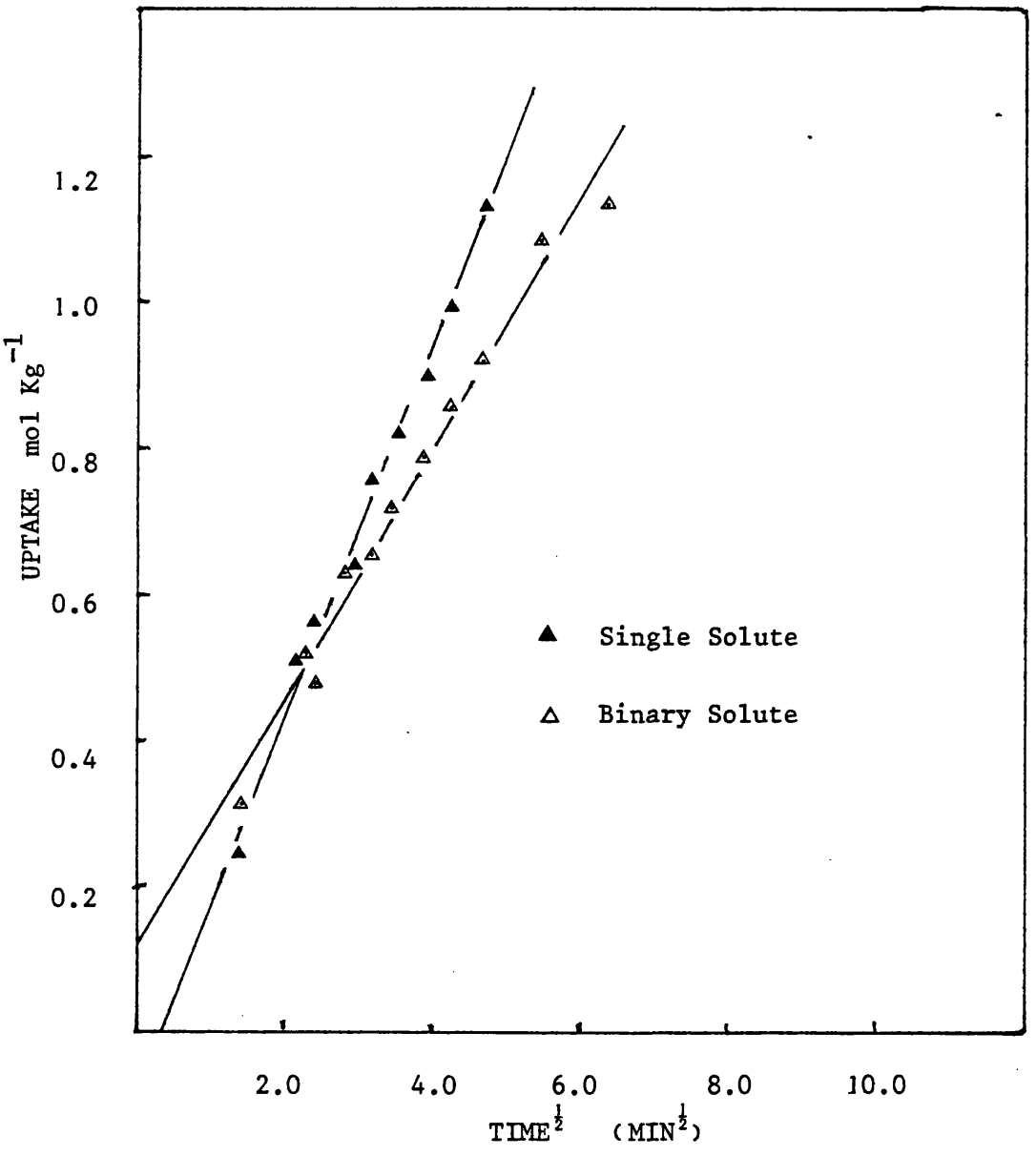


FIG 3.58 $t^{\frac{1}{2}}$ PLOTS FOR 4-NITROPHENOL ON TO 1.0 GRAMME OF ACTIVE CARBON FROM 1000ml OF BINARY SOLUTE SOLUTION CONTAINING 5×10^{-3}M 4-NITROPHENOL AND 10^{-3}M 4-METHOXYBENZOIC ACID, AND A SINGLE SOLUTE SOLUTION CONTAINING 5×10^{-3}M 4-NITROPHENOL AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o}.

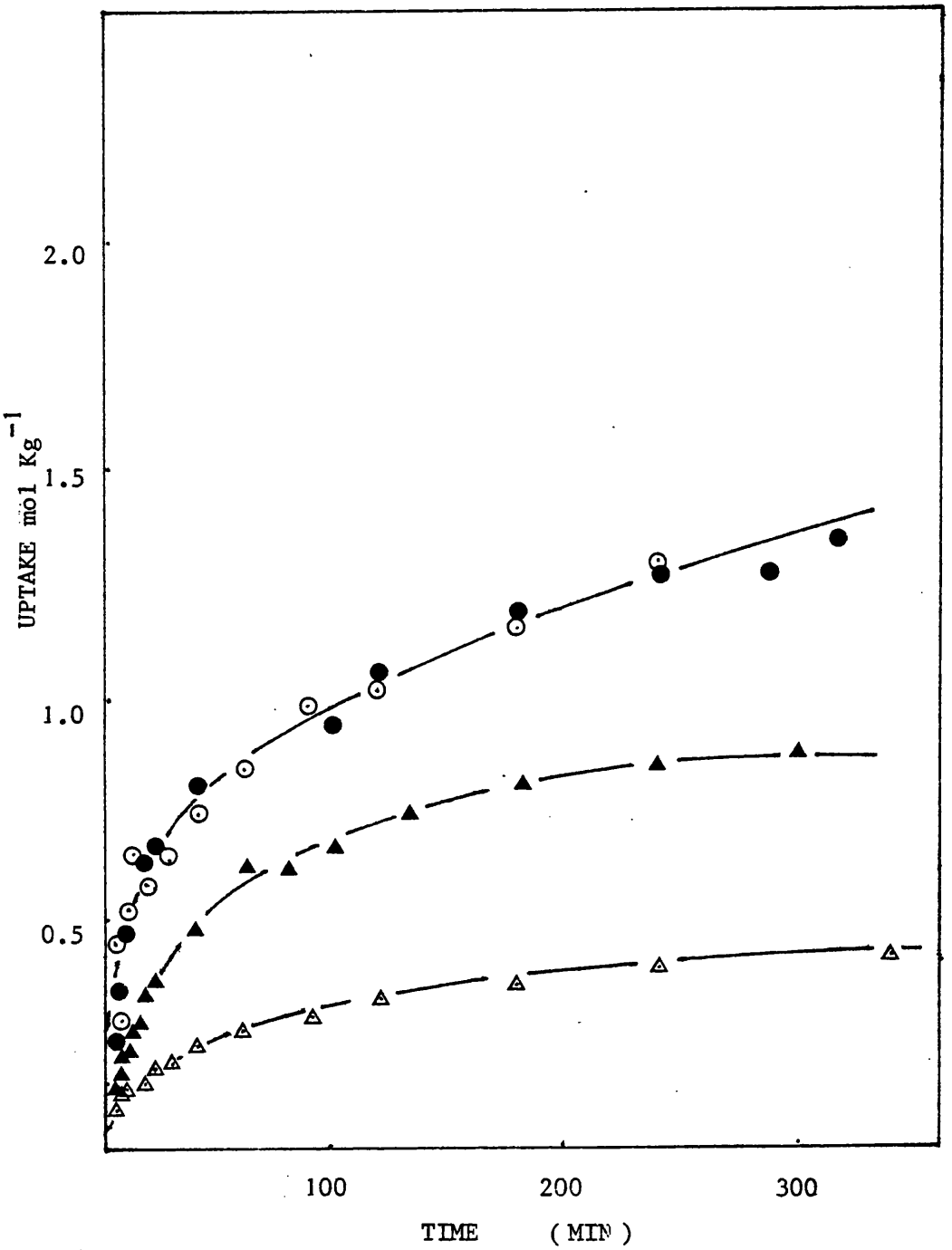


FIG 3.59 KINETIC PROFILES FOR THE SORPTION OF 4 NITROPHENOL AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF SINGLE AND BINARY SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} ON TO 1.0 gramme OF ACTIVE CARBON

KEY: ● ETHYL 4-AMINOBENZOATE; 5 x 10^{-3}M INITIAL CONCENTRATION
○ ETHYL 4-AMINOBENZOATE; 5 x 10^{-3}M + 4-NITROPHENOL; 10^{-3}M
▲ 4-NITROPHENOL ; 10^{-3}M INITIAL CONCENTRATION
△ 4-NITROPHENOL; 10^{-3}M + ETHYL 4-AMINOBENZOATE; 5 x 10^{-3}M

these solutes on nylon 6 coated carbon shows that ethyl 4-amino-benzoate rate is now affected by the presence of 4-nitrophenol, whereas, the suppression of rate of 4-nitrophenol appears to have been reduced (Figure 3.60).

The same binary solute system, with the initial concentrations reversed, is shown in figure 3.61. The kinetic profiles for the binary solute system are both reduced with respect to the single solute profiles on the uncoated carbon sorbent. Figure 3.62 showing the profiles for nylon 6 coated carbon, indicates that the rate suppression effect for 4-nitrophenol on the uncoated material is virtually abolished. The sorption profile of ethyl 4-amino-benzoate remains lowered after application of the coat, in the presence of 4-nitrophenol.

3.4.5.2. The Rate of Sorption Ethyl 4-aminobenzoate and 4-methoxybenzoic acid.

The overall rate of sorption of both solutes on active carbon is reduced (figure 3.63), however, the rate of ethyl 4-amino-benzoate is only affected slightly whereas a significant reduction in uptake takes place for 4-methoxybenzoic acid. Figure 3.64 reveals that the overall pattern of rate suppression is similar on the coated sorbent. The rate of sorption of ethyl 4-aminobenzoate is essentially unaffected up to 80 minutes when a slight lowering in rate is apparent. The overall rate of sorption of 4-methoxybenzoic acid is suppressed from zero time.

3.4.5.3. The Rate of Sorption 4-nitrophenol and 4-methoxybenzoic acid.

Figure 3.65 shows that the kinetic profiles for the rate of sorption of 4-nitrophenol and 4-methoxybenzoic acid on active carbon indicating that the overall rate of uptake of both species is

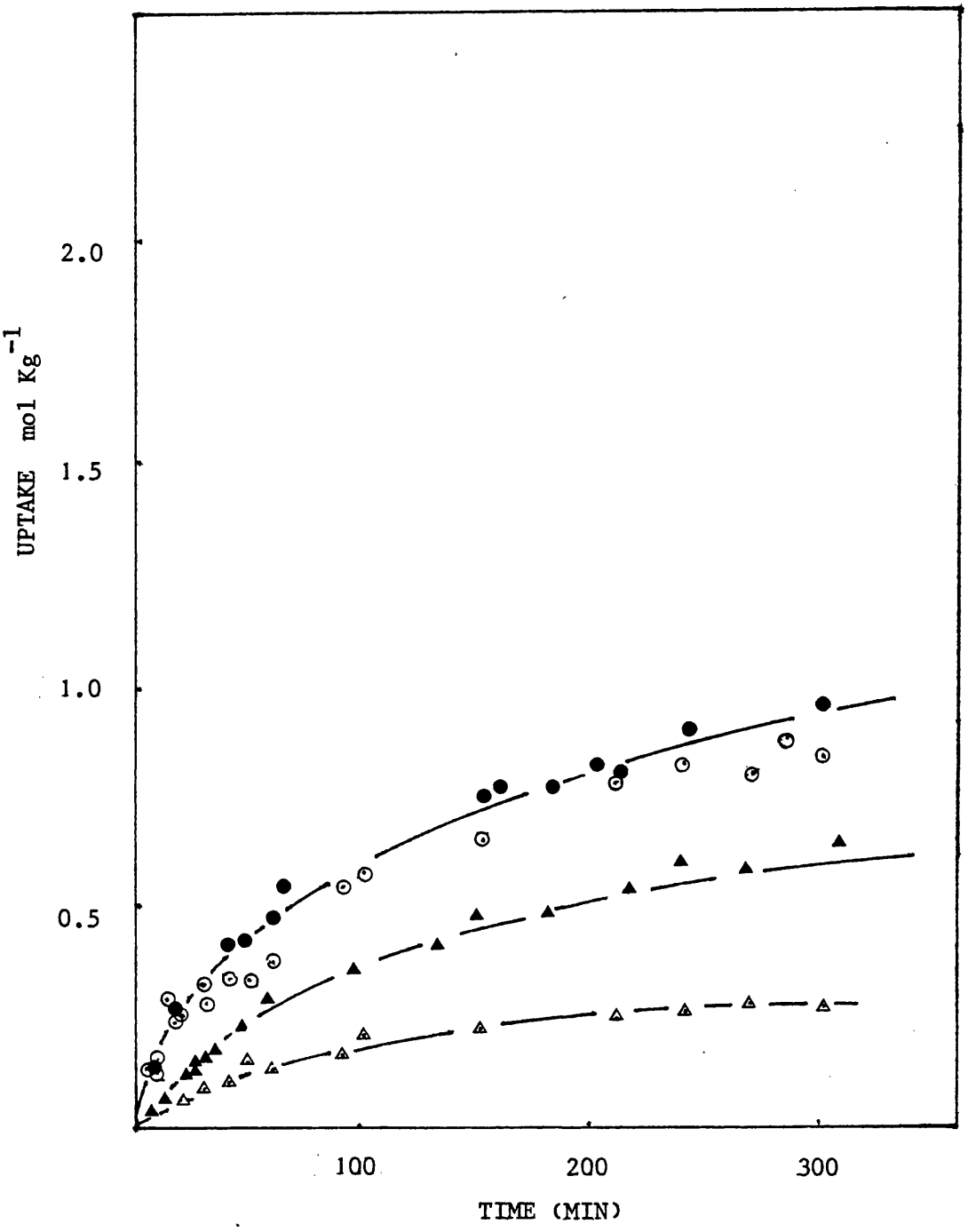


FIG 3.60 KINETIC PROFILES FOR THE SORPTION OF 4-NITROPHENOL AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF SINGLE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° ON TO 1.0 gramme OF NYLON 6 COATED ACTIVE CARBON. INITIAL CONCENTRATIONS GIVEN IN KEY BELOW.

KEY:
- ● ETHYL 4-AMINOBENZOATE: 5 x 10^{-3}M SINGLE SOLUTE.
- ○ ETHYL 4-AMINOBENZOATE: 5 x 10^{-3}M + 4-NITROPHENOL; 10^{-3}M
- ▲ 4-NITROPHENOL: 10^{-3}M SINGLE SOLUTE
- △ 4-NITROPHENOL: 10^{-3}M + ETHYL 4-AMINOBENZOATE: 5 x 10^{-3}M

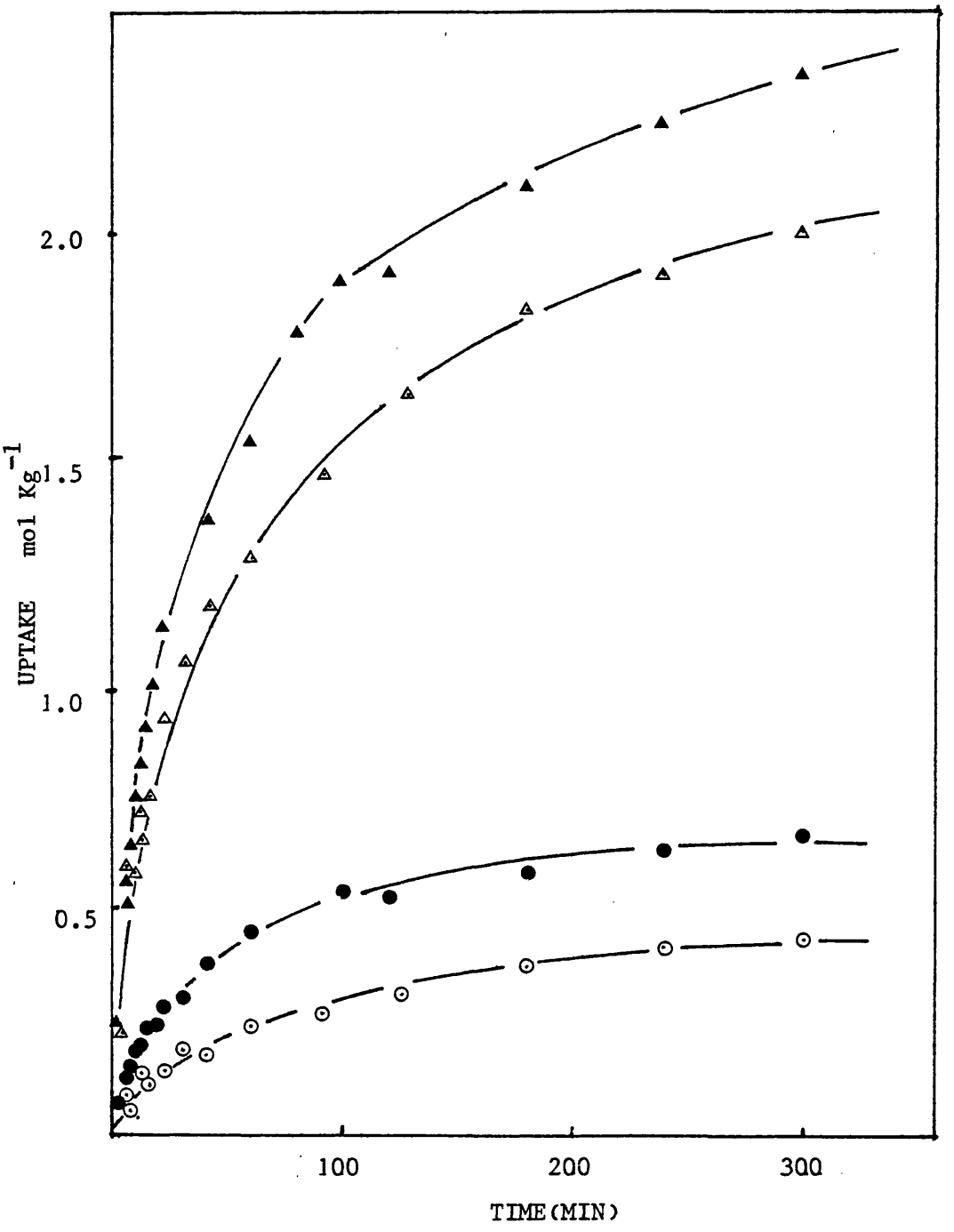


FIG 3.61 KINETIC PROFILES FOR THE SORPTION OF 4-NITROPHENOL AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF SINGLE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° ON TO 1.0 gramme OF ACTIVE CARBON. INITIAL CONCENTRATIONS GIVEN IN KEY BELOW.

KEY: ▲ 4-NITROPHENOL: 5 x 10^{-3}M SINGLE SOLUTE

△ 4-NITROPHENOL: 5 x 10^{-3}M + ETHYL 4-AMINOBENZOATE 10^{-3}M

● ETHYL 4-AMINOBENZOATE: 10^{-3}M SINGLE SOLUTE

○ ETHYL 4-AMINOBENZOATE: 10^{-3}M + 4-NITROPHENOL 5 x 10^{-3}M

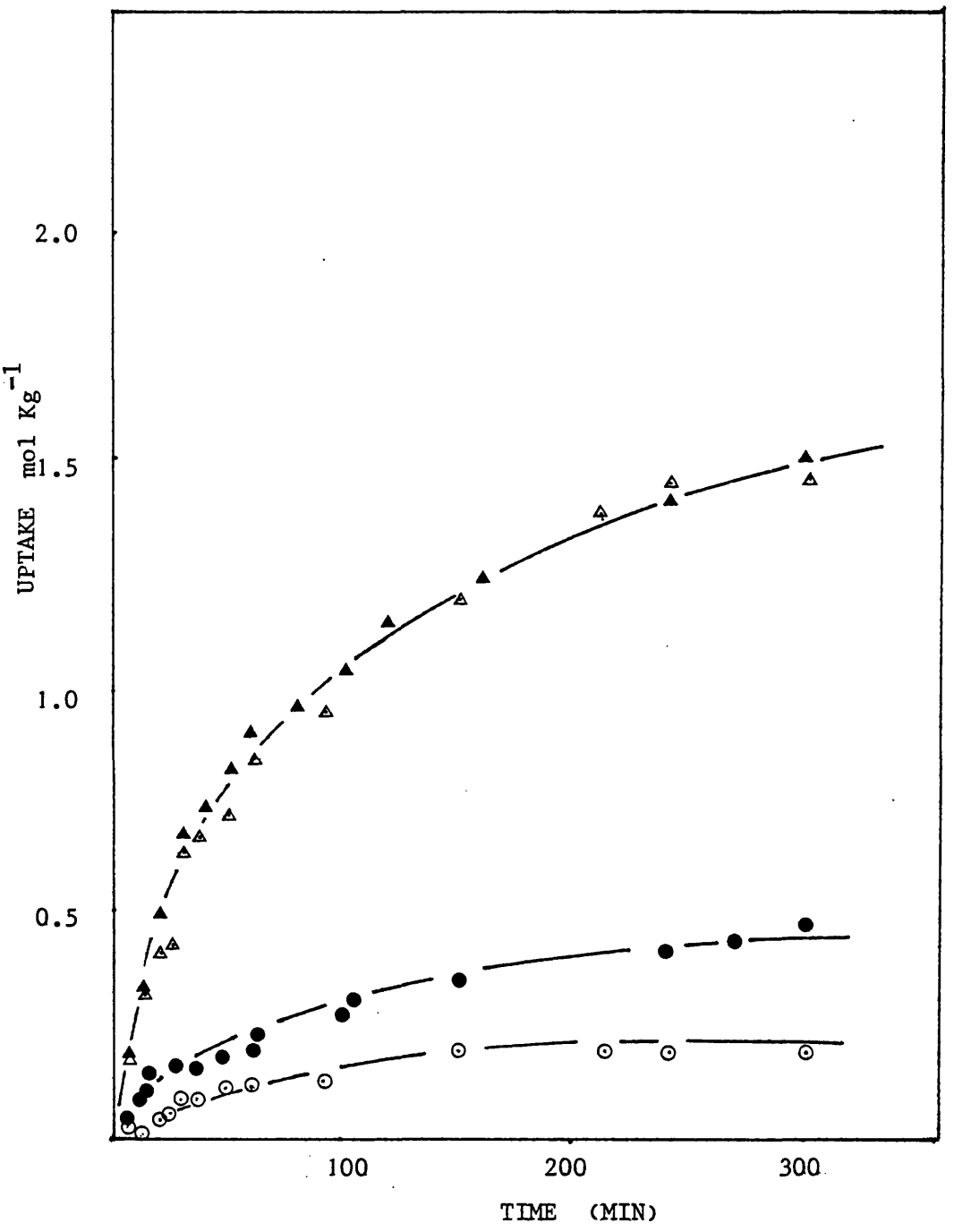


FIG 3.62 KINETIC PROFILES FOR THE SORPTION OF 4-NITROPHENOL AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF SINGLE SOLUTE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° ON TO 1.0 gramme OF NYLON 6 COATED ACTIVE CARBON. INITIAL CONCENTRATIONS GIVEN IN KEY BELOW.

KEY:
- ▲ 4-NITROPHENOL:5 x 10^{-3}M SINGLE SOLUTE
- △ 4-NITROPHENOL:5 x 10^{-3}M + ETHYL 4-AMINOBENZOATE 10^{-3}M
- ● ETHYL 4-AMINOBENZOATE: 10^{-3}M SINGLE SOLUTE
- ○ ETHYL 4-AMINOBENZOATE: 10^{-3}M + 4-NITROPHENOL 5 x 10^{-3}M

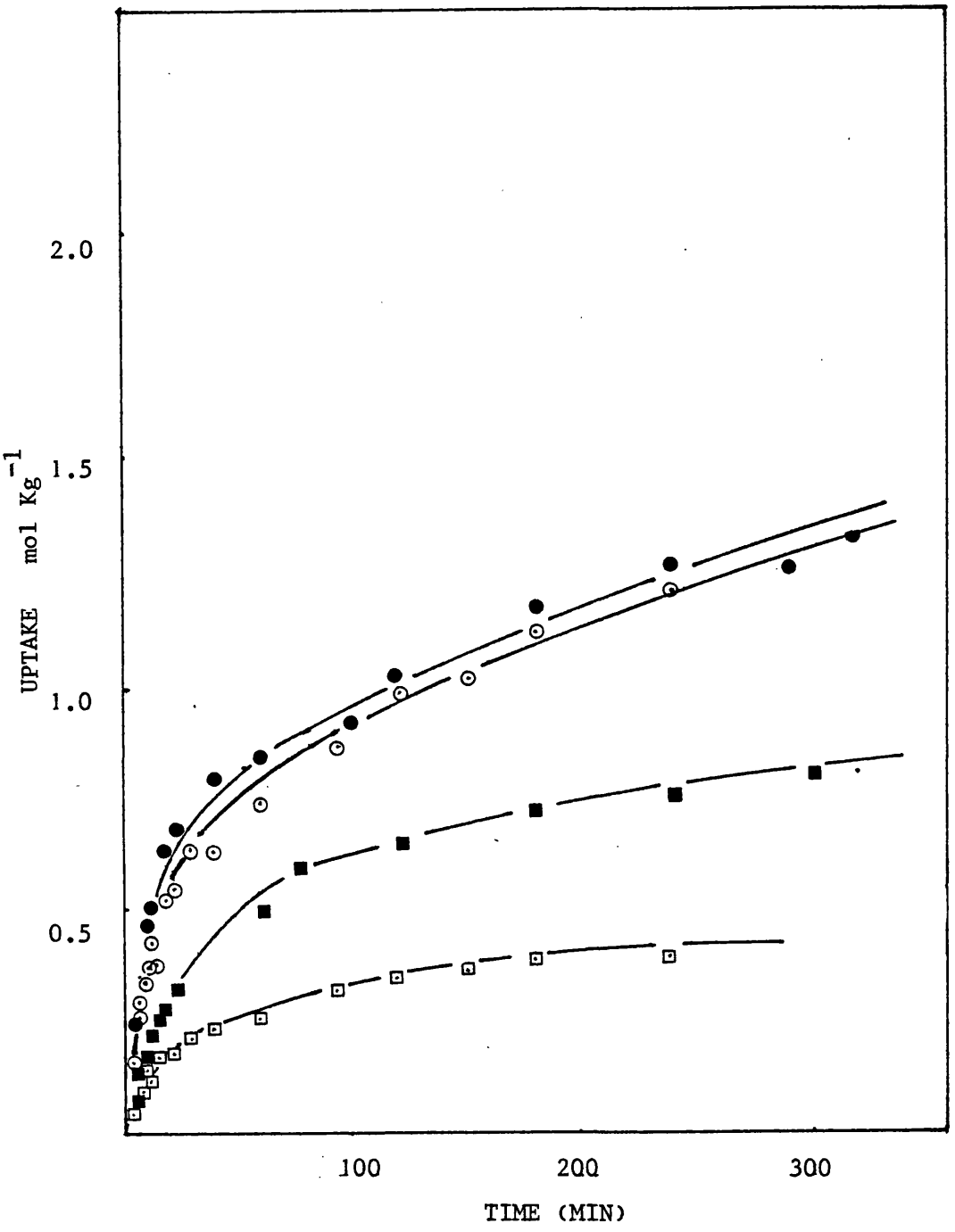


FIG 3.63 KINETIC PROFILE FOR THE SORPTION OF 4-METHOXYBENZOIC ACID AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF SINGLE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} ON TO 1.0 gramme OF ACTIVE CARBON. INITIAL CONCENTRATIONS GIVEN IN KEY BELOW.

KEY:
- ● ETHYL 4-AMINOBENZOATE 5 x 10^{-3}M SINGLE SOLUTE
- ○ ETHYL 4-AMINOBENZOATE 5 x 10^{-3}M + 4-METHOXYBENZOIC ACID 10^{-3}M
- ■ 4-METHOXYBENZOIC ACID 10^{-3}M SINGLE SOLUTE
- □ 4-METHOXYBENZOIC ACID 10^{-3}M + ETHYL 4-AMINOBENZOATE 5 x 10^{-3}M

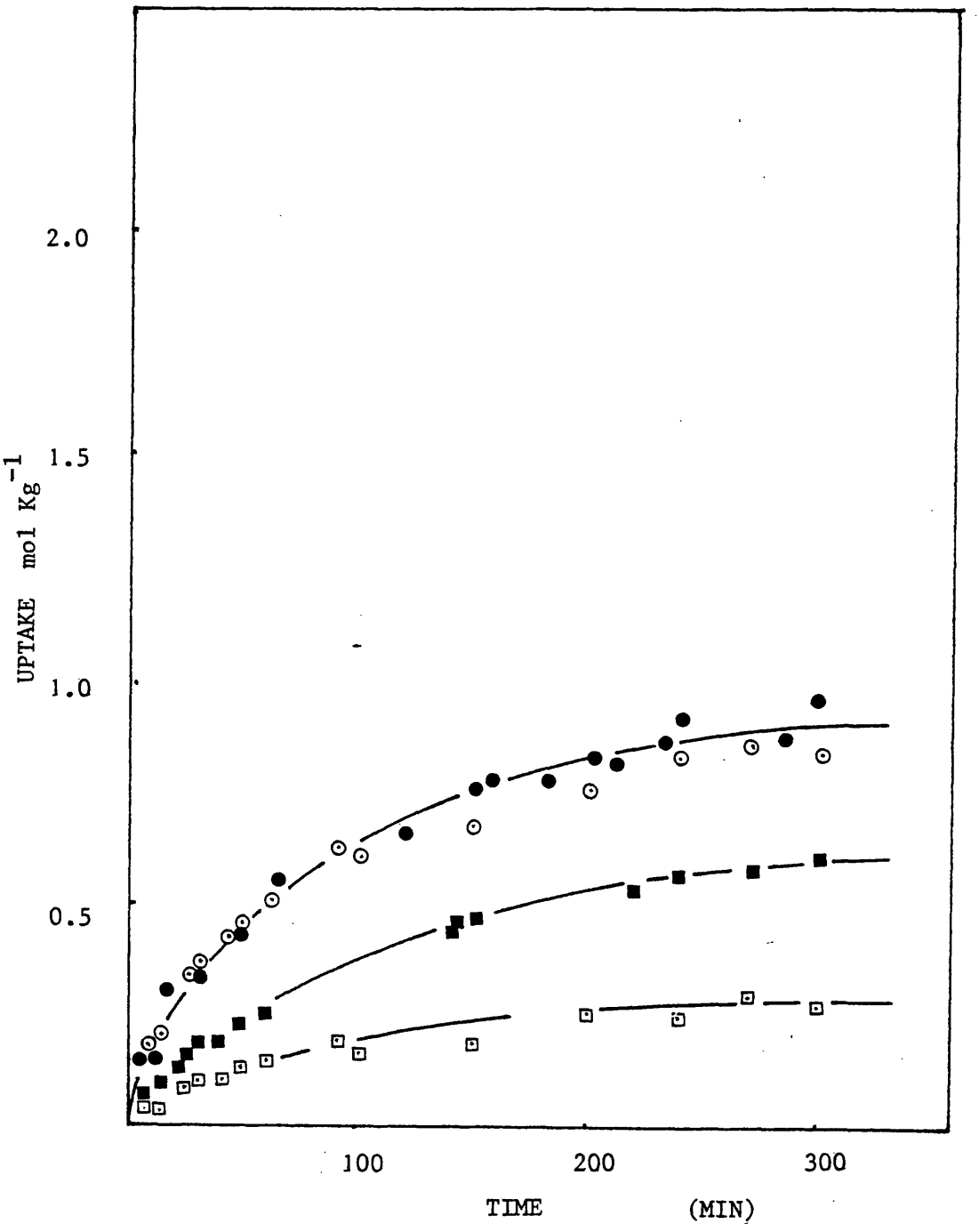


FIG 3.64 KINETIC PROFILES FOR THE SORPTION OF 4-METHOXYBENZOIC ACID AND ETHYL 4-AMINOBENZOATE FROM 1000ml OF SINGLE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5 M IONIC STRENGTH) AND 30^{o} ON TO NYLON 6 COATED ACTIVE CARBON. SORBENT WEIGHT 1.0 gramme, INITIAL CONCENTRATIONS GIVEN IN KEY BELOW.

KEY:
- ● ETHYL 4-AMINOBENZOATE 5 x 10^{-3}M SINGLE SOLUTE
- ○ ETHYL 4-AMINOBENZOATE: 5 x 10^{-3}M + 4-METHOXYBENZOIC ACID 10^{-3}M
- ■ 4-METHOXYBENZOIC ACID: 10^{-3}M SINGLE SOLUTE
- □ 4-METHOXYBENZOIC ACID: 10^{-3}M + ETHYL 4-AMINOBENZOATE 5 x 10^{-3}M

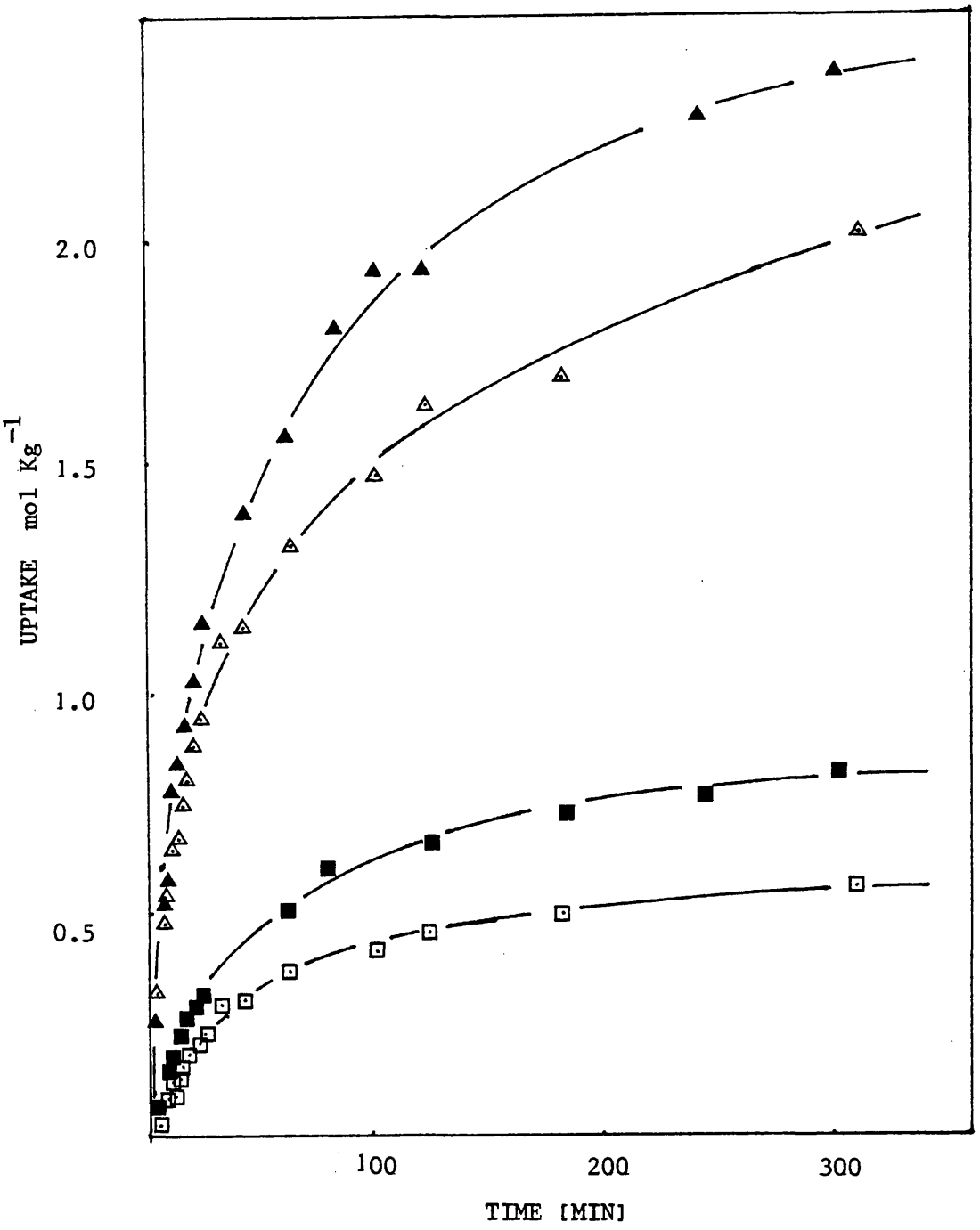


FIG 3.65 KINETIC PROFILES FOR THE SORPTION OF 4-NITROPHENOL AND 4-METHOXYBENZOIC ACID FROM 1000ml OF SINGLE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30^{o} ON TO 1.0 gramme OF ACTIVE CARBON. INITIAL CONCENTRATIONS GIVEN IN THE KEY BELOW

KEY: ▲ 4-NITROPHENOL 5 x 10^{-3}M SINGLE SOLUTE

△ 4-NITROPHENOL: 5 x 10^{-3}M + 4-METHOXYBENZOIC ACID 10^{-3}M

■ 4-METHOXYBENZOIC ACID 10^{-3}M SINGLE SOLUTE

□ 4-METHOXYBENZOIC ACID 10^{-3}M + 4-NITROPHENOL 5 x 10^{-3}M

reduced. The corresponding plot for the coated sorbent shows that the rate suppression experienced by 4-nitrophenol due to the presence of 4 methoxybenzoic acid is effectively abolished by the application of the coat. The rate profile of 4-methoxybenzoic acid remains suppressed after application of the coat. (Figure 3.66).

Full tables of kinetic data for the sorption of the model solutes by both types or sorbent from single and binary solute solution are included in Appendix 2.

3.5 DIFFUSION STUDIES OF THE MODEL SOLUTES THROUGH NYLON 6 FILM.

The diffusion and permeability of solutes through a polymer may be determined from film permeability method and the Barrer Plot discussed in Section 1.6.1.1. The diffusion and permeability coefficients of 4-nitrophenol, 4-methoxybenzoic acid and 4-amino-benzoate were determined, using a non-oriented nylon 6 film, at 30^{o} and pH 2.32 (0.5M ionic strength).

3.5.1 Determination of Barrer Plot.

Permeability cells of an all glass construction were used, which consisted of a donor and receptor compartment separated by a nylon 6 film, as shown in figure 3.67. The two compartments were tightly clamped together after lightly smearing the flange of each cell with Apiezon T grease to provide a water-tight seal. The solutions in each compartment were stirred by all glass paddle stirrers at 500 rpm shaft speed.

The donor and receptor solutions and the assembled apparatus were equilibrated to temperature in a water bath before each experiment. The solutions were then poured simultaneously into their respective compartments, at the same rate, to avoid undue distension of the membrane. The donor solution consisted of a

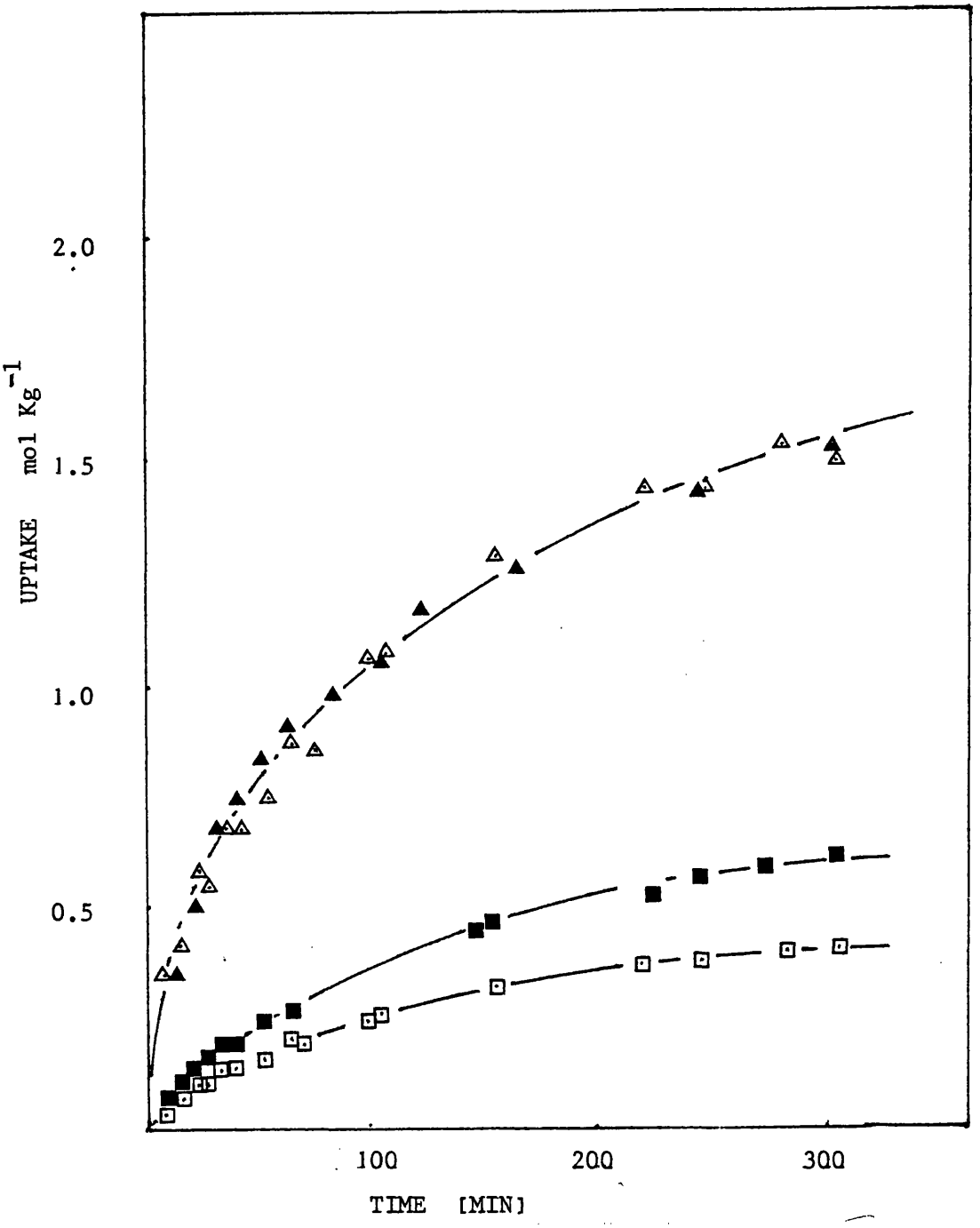


FIG 3.66 KINETIC PROFILES FOR THE SORPTION OF 4-NITROPHENOL AND 4-METHOXYBENZOIC ACID FROM 1000ml OF SINGLE AND BINARY SOLUTE SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH) AND 30° ON TO 1.0 gramme OF NYLON 6 COATED ACTIVE CARBON. INITIAL CONCENTRATIONS GIVEN IN KEY BELOW.

KEY: ▲ 4-NITROPHENOL 5 x 10^{-3}M SINGLE SOLUTE

△ 4-NITROPHENOL 5 x 10^{-3}M + 4-METHOXYBENZOIC ACID 10^{-3}M

■ 4-METHOXYBENZOIC ACID 10^{-3}M SINGLE SOLUTE

□ 4-METHOXYBENZOIC ACID 10^{-3}M + 4-NITROPHENOL 5 x 10^{-3}M

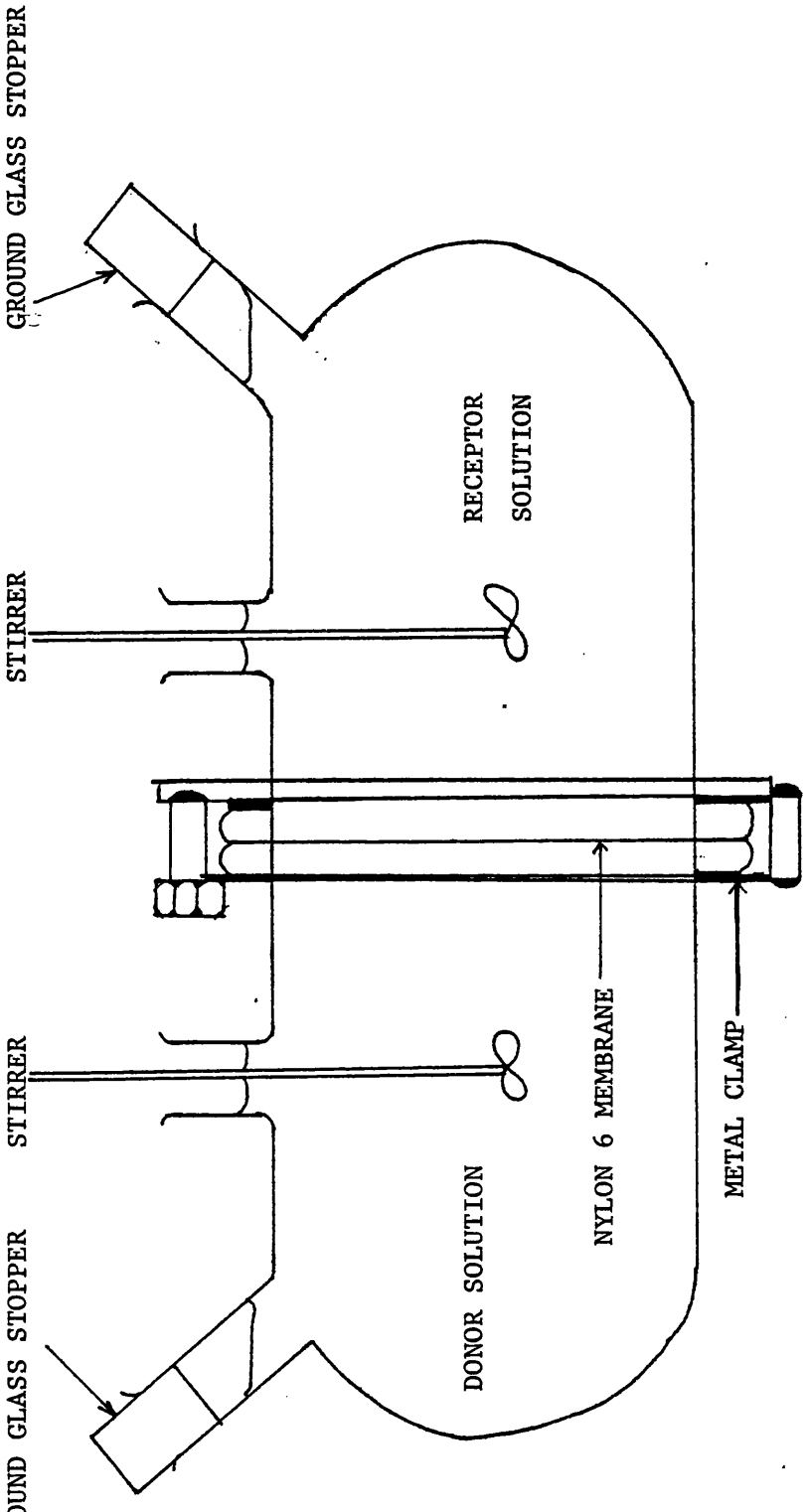


FIGURE 3.67 SCHEMATIC REPRESENTATION OF THE PERMEABILITY CELL

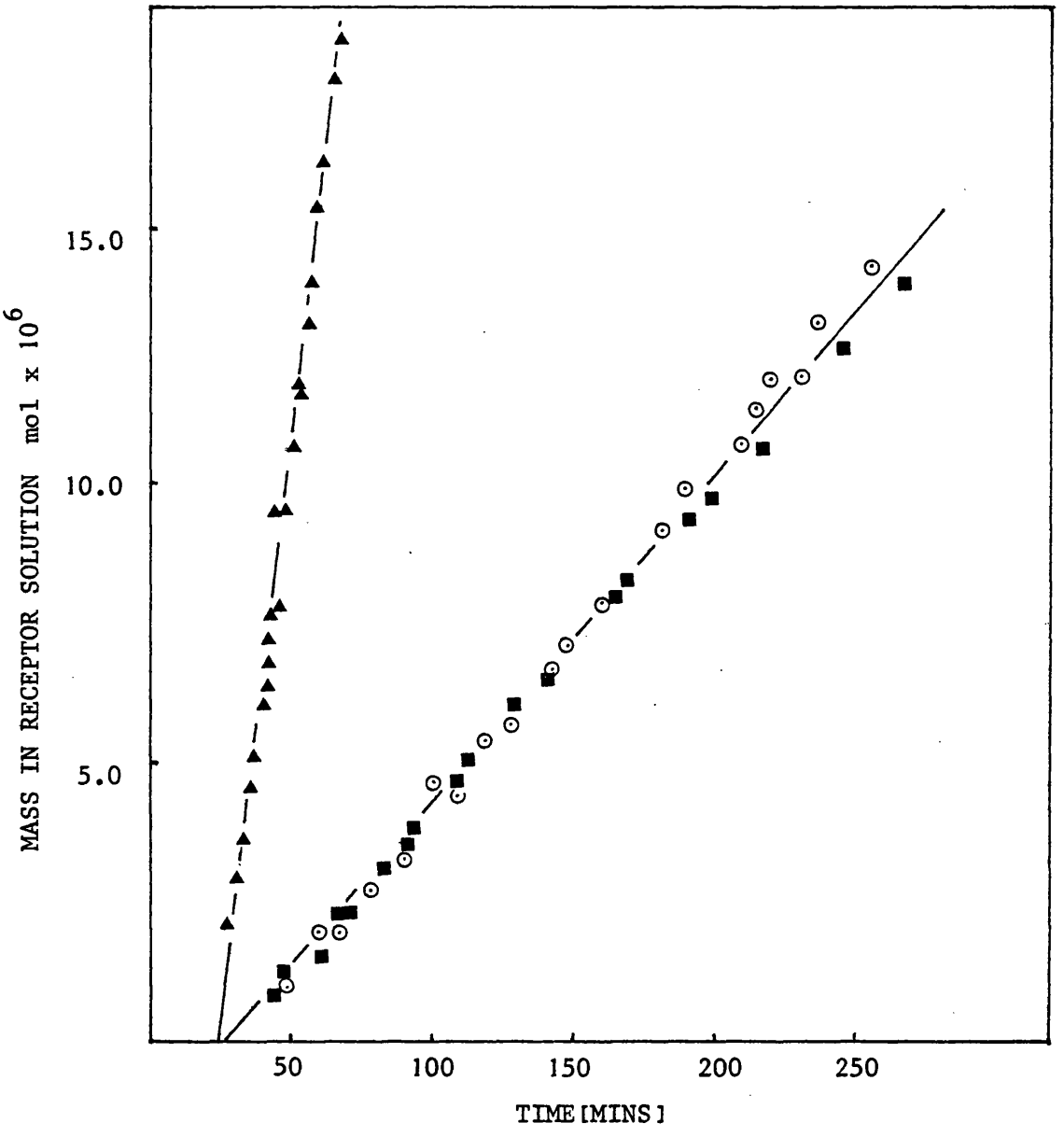


FIG 3.68 BARRER PLOTS FOR THE PERMEATION OF 4-NITROPHENOL, 4-METHOXY-BENZOIC ACID AND ETHYL 4-AMINOBENZOATE THROUGH A 30.82 μm NON-ORIENTED NYLON 6 FILM AT 30° FROM AQUEOUS SOLUTION AT pH 2.32 (0.5M IONIC STRENGTH)

KEY: ▲ 4-NITROPHENOL (INITIAL CONCENTRATION 5.08 x 10^{-3}M)

■ ETHYL 4-AMINOBENZOATE (INITIAL CONCENTRATION 5.01 x 10^{-3}M)

○ 4-METHOXYBENZOIC ACID (INITIAL CONCENTRATION 1.01 x 10^{-3}M)

solution of the appropriate solute and the receptor solution was the buffer solution without solute.

The donor solute solution was assayed spectrophotometrically prior to the commencement of the experiment to establish the initial concentration of the solute. 4 ml samples of the receptor solution were removed at intervals of time for immediate assay and were then returned to that compartment in order to maintain the receptor phase volume throughout the experimental determination. The permeation process was allowed to continue until steady-state conditions had been reached indicated by the presence of at least ten data points on the Barrer Plot which lay on a straight line. Sink conditions were essentially maintained throughout the experiment by maintaining the receptor solution concentration below 1% of that in the donor compartment.

Previous studies with blown nylon 6 films have indicated that leaching of substances from the membrane does not occur to an extent where errors are introduced into the spectrophotometric assay and that mass transfer via pinholes does not occur. (Ho. 1977).

3.5.2 Membrane Thickness and Compartment Volumes.

The thickness of the nylon 6 film was determined by subdividing the membrane in $1cm^2$ areas and the film thickness in each area measured using an electronic micrometer (Ho 1977). The thickness of the film determined from the sum of 25 random determinations of the six membranes used in the study was 30.82 μm (S.D 0.65μm).

It has been shown that there is no significant difference between the mean thickness of a blown film of non-oriented nylon 6 (Ho, 1977) and that wet and dry film thicknesses are also not significantly different for nylon 6 membranes (Ho 1977).

The capacity and permeation area of each cell were also determined, the latter from the internal cross sectional diameter measured at four points on the circumference of the aperture of each half cell. The mean value for the area of the half cell of smallest area was determined to be $8.15 \times 10^{-3}\ m^2$ (S.D.$0.004 \times 10^{-3}\ m^2$, $n=4$). A volume of 1.8ℓ was used in each cell throughout the determinations.

Treatment of Results.

Barrer plots of solute mass in the receptor compartment versus time were constructed for each experiment and the data corresponding to the steady-state region submitted to a linear least-squares regression analysis by computer. The steady state slopes of the Barrer plots for 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate are shown in figure 3.68 and the corresponding regression data is given in table 3.48.

Comparison of the slopes for each solute using a t-test indicates that the replicate determinations of the Barrer plot were satisfactorily reproducible. Comparison of the slopes of the Barrer plots shows that 4-nitrophenol has a much higher permeation rate than ethyl 4-aminobenzoate from a nominal 5×10^{-3} M solution. The rates of permeation of ethyl 4-aminobenzoate from this concentration and 4-methoxybenzoic acid from a 10^{-3} M initial concentration are similar, the latter having a slightly slower rate. The lag-time, $\bar{D}$ and P values are summarised in table 3.49. Table 3.49 indicates that the diffusion coefficients for the three solutes all have a similar order of magnitude, however, 4-nitrophenol has a value of $\bar{D}$ which is approximately 20% lower than the other two solutes, which have similar values. The P values establish the rank order of permeability as follows.

4-nitrophenol > 4-methoxybenzoic acid > ethyl 4-aminobenzoate

Table 3.48 Barrer Plot Data for the Permeation of 4-nitrophenol, ethyl 4-aminobenzoate and 4-methoxybenzoic acid Through a Non-oriented Nylon 6 Film (30.82 μm in thickness) at pH 2.32 (0.5M ionic strength) and 30°.

Solute	Initial Concentration $x10^{3}$ M	Slope $x10^{8}$ Min^{-1}	Standard Deviation of Slope $x10^{8}$ Min^{-1}	t_{calc}*	Intercept $x10^{6}$ M	Standard Deviation of Intercept $x10^{6}$ M	t_{calc}*	Correlation Coefficient
4-nitrophenol	5.08	39.90	0.90	0.03	-9.72	0.44	0.33	0.997
	5.08	39.86	0.86		-9.70	0.43		0.998
ethyl 4-amino-benzoate	5.01	6.05	0.10	0.35	-1.80	0.14	0.81	0.999
	5.01	6.10	0.10		-1.96	0.14		0.999
4-methoxybenzoic acid	1.01	5.77	0.06	1.15	-1.64	0.09	0.71	0.999
	1.01	5.68	0.05		-1.73	0.09		0.999

* $t_{tab(P=0.05)} = 2.12$ (n=10)

Table 3.49 Lag-time, Diffusion coefficient and Permeability Coefficients for the Permeability of 4-nitrophenol, ethyl 4-aminobenzoate and 4-methoxybenzoic acid Through Non-Oriented Nylon 6 Film (30.82 μm thickness) at pH 2.32 (0.5m ionic strength) and 30^{o}.

Solute	Lag-time (minutes)	$\bar{D}$ $\times 10^{13}$ m^2 sec^{-1}	P $\times 10^{12}$ m^2 sec^{-1}
4-nitrophenol	24.4	1.08	4.95
	24.3	1.09	4.95
4-methoxybenzoic acid	28.4	0.93	3.60
	30.5	0.87	3.54
ethyl 4-aminobenzoate	29.8	0.89	0.76
	32.1	0.82	0.77

3.6 SOLUBILITY DETERMINATIONS OF THE MODEL SOLUTES IN AQUEOUS SOLUTIONS.

The apparatus used for determining the solubilities of the model solutes is shown in figure 3.69. About 30ml of buffer solution was placed in the inner vessel together with an excess amount of solute to ensure that a saturated solution would eventually result. The water in the outer vessel was supplied from a thermostatted water bath. The circulating water in the outer vessel was raised to 70^{o} for 1 hour, and allowed to equilibrate. The time interval of 1 hour has been previously shown to be sufficient for equilibration (Richardson 1973). Samples of the supernatant solutions of ethyl 4-aminobenzoate and 4-methoxybenzoic acid were removed via a sinter tube (No.3 porosity) which was preheated to the experimental temperature to avoid crystallisation of solute during sampling. A similar method was adopted for phenol and 4-nitrophenol where phenol-water systems at all temperatures and 4-nitrophenol-water systems at higher temperature formed two immiscible liquid layers. In both cases the upper, solvent rich layer was sampled.

The sample solution was transferred to a tared 150ml nominal capacity glass, stoppered flask which contained exactly 50ml of analytical buffer. After introduction of the sample, the flask was reweighed and the resulting solution was assayed spectrophotometrically. The density of the saturated solution was also determined, to enable the molar concentration of the saturated solution to be calculated from the sample weight, and spectrophotometric assay. Two replicate determinations of the solubility of each solute at the appropriate pH over the temperature range

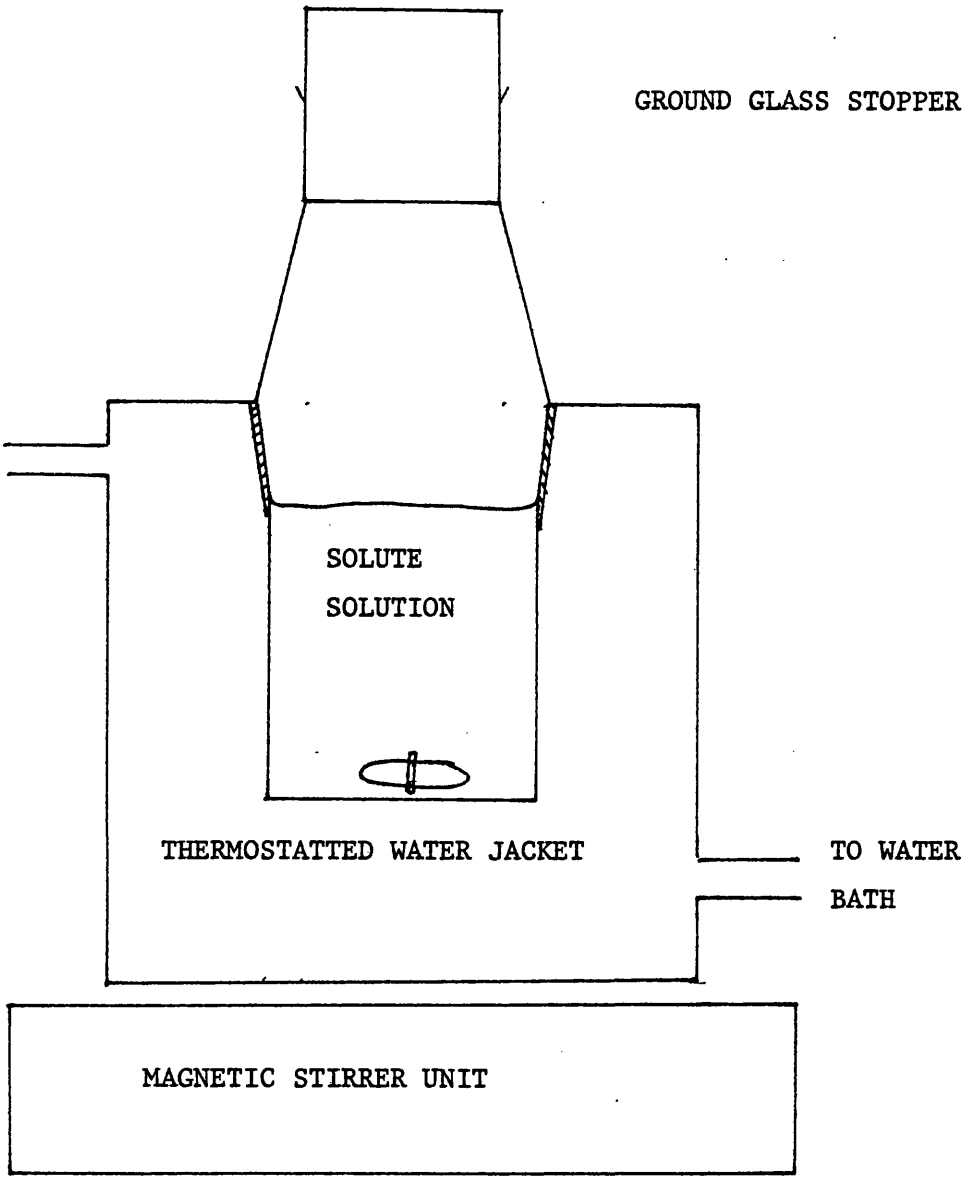


FIGURE 3.69: SCHEMATIC REPRESENTATION OF THE SOLUBILITY DETERMINATION APPARATUS.

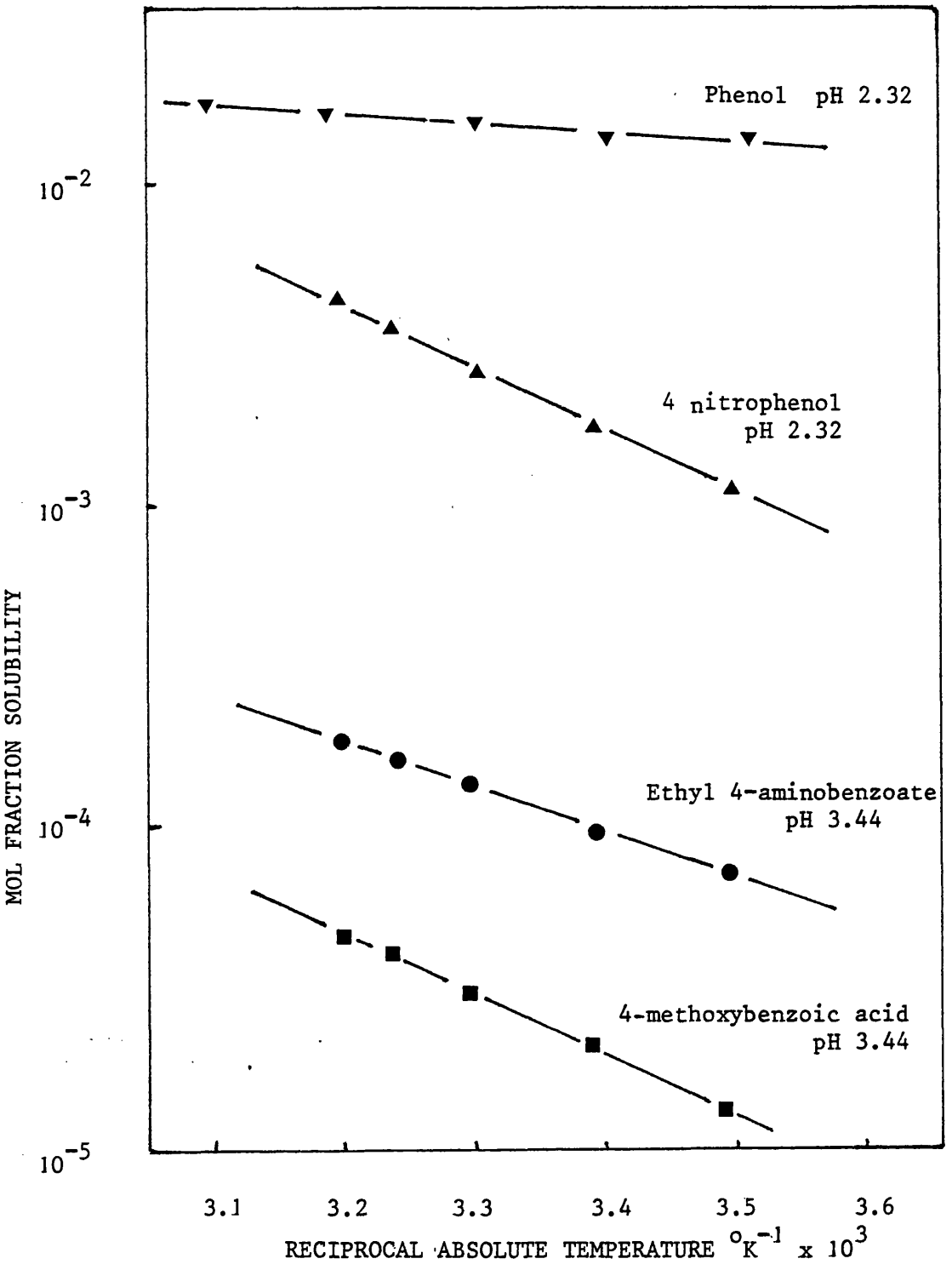


FIG 3.70 VAN'T HOFF ISOCHORES FOR THE AQUEOUS SOLUBILITY OF 4-NITROPHENOL, PHENOL, 4-METHOXYBENZOIC ACID AND ETHYL 4-AMINOBENZOATE AT 0.5M IONIC STRENGTH

10^{o}-40^{o} are given in table 3.50 as mole fraction and shown plotted as Van't Hoff isochores in figure 3.70.

Treatment of Results.

If the solid and solution phases in equilibrium at the saturation solubility are expressed with respect to the standard state of unit mole fraction the free energy change associated with dissolution is given by equation 3.11.

$$\Delta G^{o}_{s} = -RT \ln \chi \qquad \text{.....(3.11)}$$

where ΔG^{o}_{s} = the standard free energy of the dissolution process

χ = the mole fraction of solute in saturated solution

R = the gas constant

T = absolute temperature.

Figure 3.70 shows that the plots of log solubility versus reciprocal absolute temperature were linear and the data was submitted to a linear least-squares regression analysis. The slope of the Van't Hoff plot was used to obtain ΔH^{o}_{s}, the standard enthalpy associated with the dissolution process (equation 1.9). The standard entropy was then obtained from(Gibb's equation 1.11). Thermodynamic data for the solubility of the four model solutes is given in table 3.51.

Table 3.50 Solubility Data for the Four Model Solutes in Aqueous Buffer Solution at Ionic Strength 0.5M.

Solute	pH	$1/x10^{3}$ $T^{o}A$	Molar Concentration		Density $g\ cm^{-3}$	Mole Fraction	
			1	2		1	2
			$x10^{2}$ M			$x10^{3}$	
4-nitrophenol	2.32	3.490	6.01	6.09	1.033	1.11	1.12
		3.387	9.57	9.56	1.033	1.77	1.77
		3.295	13.88	13.90	1.035	2.58	2.58
		3.197	23.13	23.30	1.036	4.35	4.38
		3.232	18.97	19.08	1.036	3.55	3.57
			x10M			$x10^{2}$	
phenol	2.32	3.510	7.08	6.87	1.068	1.32	1.28
		3.400	7.23	7.30	1.054	1.37	1.39
		3.300	7.84	8.08	1.046	1.51	1.56
		3.191	8.26	8.19	1.040	1.60	1.59
		3.094	8.90	8.90	1.037	1.74	1.74
			$x10^{4}$M			$x10^{5}$	
4-methoxybenzoic acid	3.44	3.490	7.22	7.06	1.030	1.33	1.30
		3.387	11.46	11.67	1.031	2.11	2.15
		3.295	16.28	16.29	1.030	3.04	3.01
		3.197	24.97	24.52	1.030	4.61	4.53
		3.232	21.81	21.59	1.031	4.03	3.98

Continued.....

Table 3.50 Continued ...

Solute	pH	$1/x10^3$ T^oA	Molar Concentration 1	2	Density $g\ cm^{-3}$	Mole Fraction 1	2
			$x10^3$ M			$x10^5$	
ethyl 4-aminobenzoate	3.44	3.490	3.82	3.85	1.031	7.05	7.11
		3.387	5.37	5.37	1.031	9.92	9.92
		3.295	7.46	7.45	1.031	13.78	13.78
		3.197	10.01	10.13	1.030	18.52	18.74
		3.232	8.99	9.00	1.030	16.63	16.64

Table 3.51 Thermodynamic Data for the Solubility of the Four Model Solutes in 0.5M Ionic Strength Aqueous Buffer Solution.

Solute	pH	ΔH^{o}_{s} $KJmol^{-1}$	ΔG^{o}_{s} * $KJmol^{-1}$	ΔS^{o}_{s} * $Jdeg^{-1}mol^{-1}$	Temperature Range
4-nitrophenol	2.32	+38.13(±1.0) +38.10(±1.1)	+15.01 +15.01	+ 76.30 + 76.20	10 - 40
phenol	2.32	+5.64(±0.4) +5.97(±0.7)	+10.56 +10.48	- 16.24 - 14.88	10 - 50
ethyl 4-aminobenzoate	3.44	+35.21(±1.0) +35.21(±0.5)	+26.20 +26.23	+ 29.74 + 29.64	10 - 40
4-methoxybenzoic acid	3.44	+27.59(±0.46) +26.60(±0.37)	+22.40 +22.40	+ 17.13 + 17.16	10 - 40

* Calculated at 30^{o}

SECTION 4

DISCUSSION

4.1 SINGLE SOLUTE SORPTION BEHAVIOUR..

4.1.1 THE MORPHOLOGICAL and PHYSICAL CHARACTERISTICS of the NYLON 6 POWDER and GRANULAR ACTIVE CARBON.

4.1.1.1 Nylon 6 Powder.

Solvent extraction of the nylon 6 powder sample, using water and 95% v/v ethanol, did not reveal the presence of significant amounts of ultra violet absorbing contaminants such as synthetic modifiers or monomers (Section 2.6.2.2). The absence of a strong band at 870 cm^{-1} in the infra-red absorption spectrum of the powder further indicates that the amount of unreacted monomer in the sample was small (figure 2.1). The surface areas of the 60 mesh 60 - 120 mesh and sub 120 mesh powder samples were found to be 5.1, 3.7 and 4.3 $m^2 g^{-1}$ respectively, as determined by krypton gas adsorption (Section 2.6.2.5). These values suggest that the nylon 6 powder sample has a low adsorptive capacity as compared to active carbons which have values of surface areas in excess of 1000 $m^2 g^{-1}$. As these three values represent such small surface areas and no relationship between surface area and particle size is apparent, the differences in the values probably reflect errors in the determination and are, as such, not significant. The low values of surface area indicate that molecular size pores (micropores) are not present. This conclusion is supported by data from the mercury porosimetry study which showed low pore volumes of 7.1×10^{-2} $cm^3 g^{-1}$ and 4.1×10^{-2} $cm^3 g^{-1}$ for the 60 mesh and sub 60 mesh size fractions respectively. The pore size distribution in the nylon 6 powder shows that about 11% of its pore volume is in the upper transitional pore region and 89% in the macro pore region. The porograms for the samples of nylon 6 appear to level out as they approach the absissa tending to become parallel to it. (Figure 2.5).

This indicates that the pore network does not extend into the micropore size range, which conflicts with the scanning electron microscope studies of Richardson (1973) suggesting that nylon 6 powder, formed by precipitation from formic acid solution, was highly porous in nature.

The density of the nylon 6 powder was found to be 1.17 g cm^{-3} determined by a helium displacement method, corresponding to a crystallinity of approximately 50 - 60% (Encyclopedia of Polymer Science). The crystallinity of nylon is generally high due to the ability of the polymer chains to form hydrogen bonds with one another. The extent of crystallinity is also affected by other environmental factors such as temperature and physical stress (Lord 1974). This true density value would suggest that the crystallinity of the sample is moderately low. Richardson (1973) reported a low value of 10-15% crystallinity for nylon 6 powder produced by the same method. The infrared spectrum shows that the nylon 6 powder consists of the α form together with the δ form (Richardson 1973). The viscosity average molecular weight of the 60 mesh powder was found to be 26,900 which is similar to values of 28,900 and 32,800 determined for nylon 6 by Richardson (1973).

Scanning electron microscopy studies showed that the surface of the powder was highly convoluted resembling the appearance of coral as described by Richardson (1973) (plate 4.1).

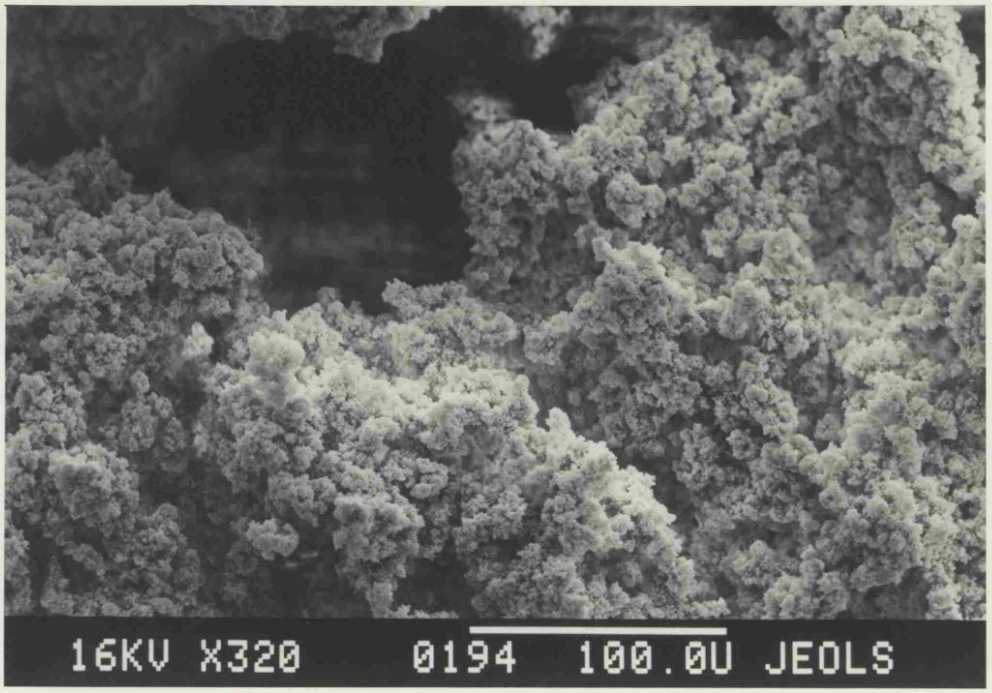


Plate 4.1 Nylon 6 Powder x 815 Magnification (⟵ 100μm ⟶).

It would appear, therefore, that the nylon 6 powder used in these studies consists of a chemically pure, non porous, highly crystalline material that has a surface area of about 4 m^2g^{-1} and a viscosity average molecular weight of about 27,000.

4.1.1.2 Active Carbon.

No significant amount of ultraviolet absorbing species were found after extraction with water and 95% v/v aqueous ethanol (Section 2.7.3.1). The surface area of the carbon is extremely high and is of the order of 1200 - 1500 m^2g^{-1} as measured by nitrogen gas and benzene vapour adsorption (Section 2.7.1). The pore volume measured by mercury porosimetry was 0.269 cm^3g^{-1} which is four times that of the nylon 6 powder and suggests that this sorbent is highly porous in nature. Of this total pore volume that can be measured by the penetration of the mercury, 50% was present in the macropore region and 20% in the transitional pore region. The pore size

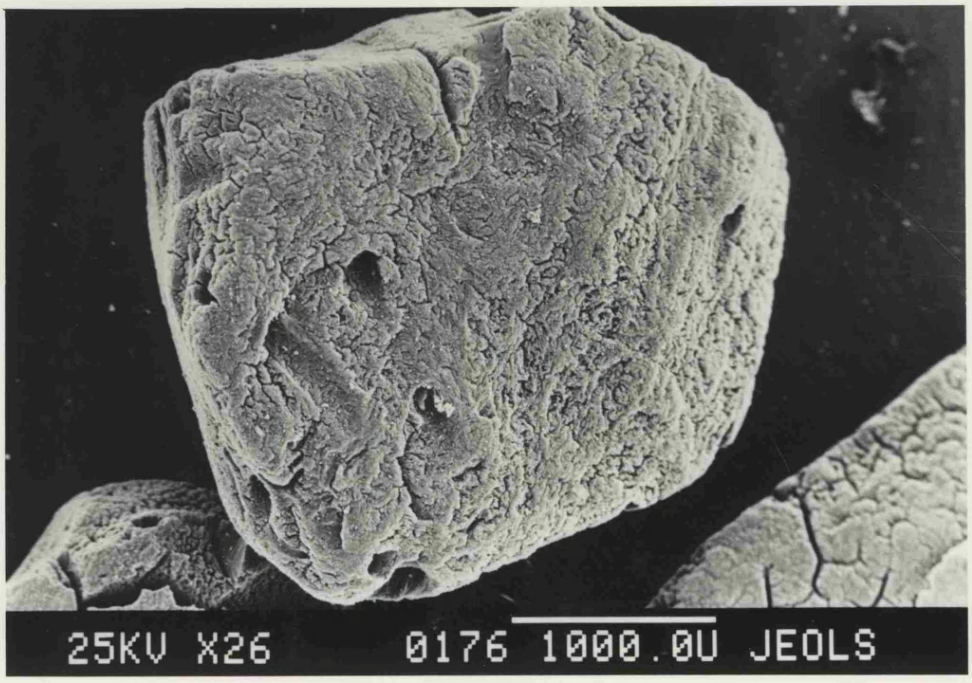


Plate 4.2 Active Carbon x 66 Magnification.

(1000μm)

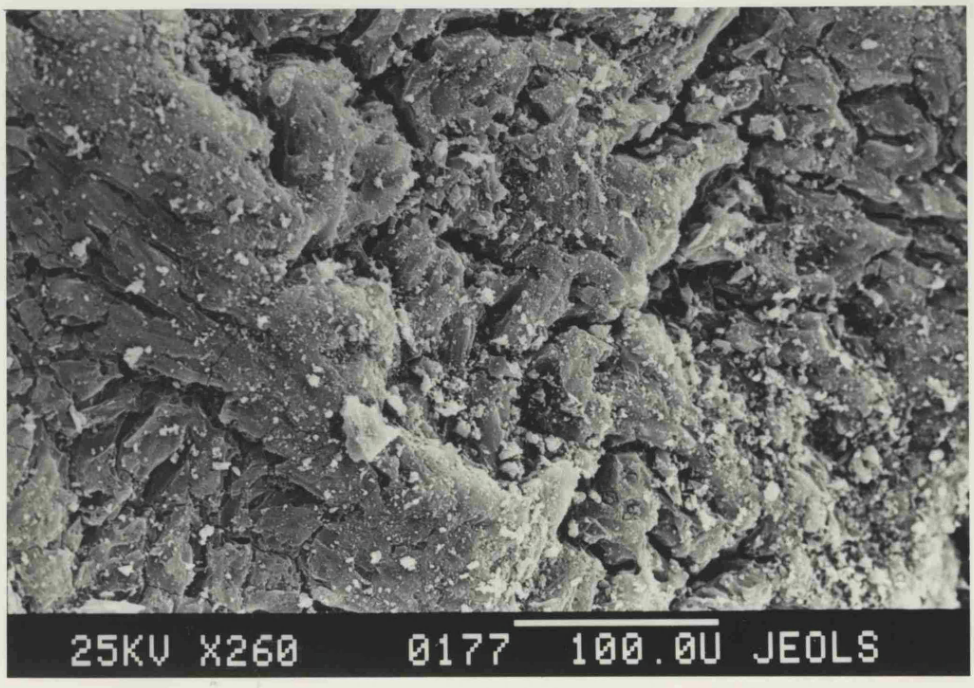


Plate 4.3 Active Carbon x 662 Magnification. (100 μm)

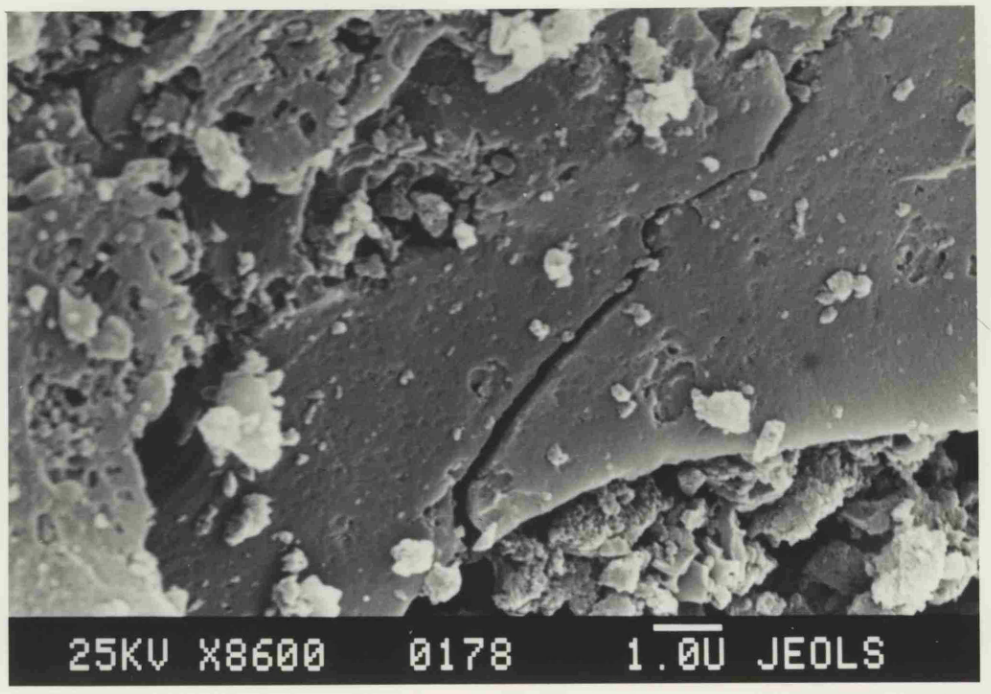


Plate 4.4 Active Carbon x 21,900 magnification.

(1 μm)

distribution for active carbon granules (figure 2.7) shows an intercept on the abscissa indicating that the sorbent is microporous in nature.

Heats of wetting and saturation vapour uptake data show that no molecular sieve effect is present up to a molecular weight of 153.8 (Section 2.7.3.2). The highest model solute molecular weight used in this study was that for ethyl 4-aminobenzoate which has a value of 165.2 and it is therefore unlikely that the sorption of model solutes will be influenced by size exclusion processes.

Plates 4.2, 4.3 and 4.4 show scanning electron micrographs of the surface of the active carbon granules magnified 66, 662 and 21,900 times respectively. Under low magnification the particle shape is seen to be irregular with distinct flat faces and edges. The surface is fissured and is perforated by holes approximately 180 μm in diameter together with smaller pits. The small pits, which are the principal surface feature at times 66 magnification are seen at times 662 magnification to be small fissures approximately 20 μm in diameter. The higher magnification photo micrographs also show that a certain amount of surface debris is present as small irregular shaped particles.

4.1.2 THE CHARACTERISATION of the SORPTION PROPERTIES of NYLON 6 and ACTIVE CARBON.

4.1.2.1. Nylon 6.

4.1.2.1.1 The Equilibrium Sorption of the Model Solutes.

Sorption studies were carried out in 50 ml stoppered conical flasks and allowed to equilibrate in a thermostatted shaking water bath. The temperature fluctuation over the temperature range used ($7-70^{o}$) was $\pm 0.2^{o}$. A minimum equilibration time of 2 hours was used throughout as equilibration was achieved within one hour for all of

the model solutes (table 3.7). Richardson (1973) has shown previously that the sorption of ethyl 4-aminobenzoate from aqueous solution by nylon 6 powder was rapid; maximum uptake occurring within 2-3 minutes in a stirred system.

The general experimental method used to obtain sorption isotherm data was validated by studying the interaction of ethyl 4-aminobenzoate from aqueous solution by nylon 6 powder. Figure 3.6 shows a typical isotherm which is linear over the concentration range studied ($0 - 6 \times 10^{-3}$ M). The result of subjecting the isotherm data to a least-squares regression analysis is shown in table 3.9. The intercept spans the origin within ± two standard deviations and the correlation coefficient is greater than 0.990. These two criteria were defined by Richardson (1973) for the assignment of C_1 type isotherm behaviour to a sorption system. The slope of the isotherm, the K value, was 18.6 l Kg^{-1} and this compares to a mean value from three determinations of 19.4 l Kg^{-1} reported by Richardson (1973). In most cases of sorption from single solute solutions of the model compounds, the above criteria for C_1 type linearity were met. Several systems gave rise to isotherms which did not span the origin within ± two standard deviations. For instance, the sorption of ethyl 4-aminobenzoate on to 0.4 gramme of nylon 6 powder over an initial concentration range of $0 - 5 \times 10^{-3}$ M gave an intercept of 3.06×10^{-4} mol Kg^{-1} and a standard deviation of 1.34×10^{-4} mol Kg^{-1}. As the intercepts were always small compared to the lowest observed values of uptake it was considered that these systems were of C_1 type although not strictly fulfiling the criteria of Richardson.

The sorption of ethyl 4-aminobenzoate has been shown to be influenced by many factors such as pH, ionic strength and temperature (Ho 1977, Richardson 1973). The sorption systems were therefore carefully controlled with respect to these physicochemical factors. Sorption isotherms of ethyl 4-aminobenzoate were determined using 0.1g, 0.2g, and 0.4g of nylon 6 powder (BS 60 mesh sieve size). The isotherms were all of C_1 type and their slopes were not significantly different (table 3.9). Similarly, the isotherms determined using 0.2g of nylon 6 powder of particle size fractions > 60 mesh, 60–120 mesh and < 120 mesh did not have significantly different K values (table 3.10). The sorption isotherm for ethyl 4-aminobenzoate from aqueous solution was, therefore, linear and independent of particle size and sorbent-solution volume ratio. The K value fully and unambiguously describes the sorption equilibrium, at constant temperature and specified conditions of solution composition.

Early studies on the sorption of weak aromatic electrolytes by polyamides gave rise to several conflicting reports on the type of isotherm obtained. Several workers reported L isotherm behaviour (Chipalkatti, 1954 ; Guess et al 1962; Kapadia et al 1964; Kim et al 1959) whereas others have reported C_1 type behaviour. The extensive studies of Richardson (1973) and Ho (1977) using both nylon 6 powder and a range of polyamide films showed that the interaction with ethyl 4-aminobenzoate gave linear C type isotherms in all cases. The sorption of phenol, ethyl 4-aminobenzoate and 4-methoxybenzoic acid from buffered aqueous solution all gave rise to linear C_1 type isotherms (figures 3.9, 3.7 and 3.8 respectively) over the concentration range studied. C_1 type isotherm behaviour is generally taken to indicate that the solutes are penetrating the polymer matrix as the

availability of the interaction sites appears to remain constant and independent of the amount of solute previously adsorbed. Giles (1974) has described a model which may account for such C type behaviour. The model defines an adsorbing surface with an effective "area" which expands by matrix polymer chain disentanglement under the influence of the penetrating solute molecules. The rate of adsorption is independent of the available area of substrate at any given time as each molecule generates new interaction sites as soon as it is adsorbed. The rate of desorption, or removal of the solute molecule from its sorption site, will be proportional to the area of the substrate covered by the solute which is in turn proportional to the uptake. This can be quantified as follows:

$$\text{Rate of adsorption} = k_a C_{eq} \quad \ldots\ldots\ldots \quad (4.1)$$

$$\text{Rate of desorption} = k_d n \quad \ldots\ldots\ldots \quad (4.2)$$

where k_a = the adsorption rate constant

k_d = the desorption rate constant

C_{eq} = the equilibrium concentration of solute in the liquid phase

n = the equilibrium uptake of the solute

At equilibrium

$$k_a C_{eq} = k_d n \quad \ldots\ldots\ldots \quad (4.3)$$

and

$$\frac{n}{C_{eq}} = \frac{k_a}{k_d} \quad \ldots\ldots\ldots \quad (4.4)$$

Equation 4.4 is identical in form to equation 1.7 thus the characteristic "K" value is the ratio of the adsorption and desorption rate constants.

The disentanglement of the matrix structure cannot continue indefinitely and a situation can be envisaged where the primary disentanglement at low solute uptake can give way to a secondary process. Giles (1974) considered the system described by equation 4.4 to be independent of the disentanglement process and that the rates of entanglement and disentanglement, should they become rate limiting in the overall sorption process, could influence the sorption isotherm. The overall process can be described thus:

where :

$$\underset{[\text{Solution}]}{\text{Solute}} \underset{k_{re\text{-}ent}}{\overset{k_{disent}}{\rightleftharpoons}} \underset{\text{State}}{\text{Intermediate}} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \underset{[\text{adsorbed}]}{\text{Solute}}$$

where : k_{disent} = rate constant for disentanglement

$k_{re\text{-}ent}$ = rate constant for re-entanglement

k_a = adsorption rate constant

k_d = desorption rate constant

A horizontal plateau in the isotherm would suggest that saturation of the entire area capable of being disentangled by the solute has been achieved. The disentanglement of other areas then proceeds either infinitely slowly or not at all. This situation is observed for the sorption of 4-nitrophenol by nylon 6 powder (figure 3.10) where a plateau is seen at an uptake of about 2 mol Kg^{-1}; the sorption profile for this system therefore corresponds to C_2 type behaviour. Although many cases of C_1 type isotherm behaviour have been reported for sorption by synthetic polymers there have been few cases of C_2 type behaviour. An example of the latter is the adsorption of water on to

wool from butan-1-ol (Chipalkatti 1954). The sorption of ethyl 4-aminobenzoate and 4-methoxybenzoic acid over the concentration ranges studied do not reach an uptake of 2 mol Kg^{-1} which may account for the absence of a plateau. It was necessary to use high solution concentrations and low sorbent weights to obtain C_2 type isotherm behaviour, this would probably be also necessary to obtain the same result for ethyl 4-aminobenzoate and 4-methoxybenzoic acid. This was not attempted for these two solutes which may account for the absence of the plateau at the higher limit of uptake. Phenol, however, reaches an uptake of 3.5 mol Kg^{-1} and the isotherm retains its C_1 type characteristics. It may be, therefore, that phenol interacts more strongly with the nylon 6 matrix allowing it to penetrate regions of the polymer which are inaccessible to 4-nitrophenol.

The nature of the interaction mechanism between organic solutes and polyamides has been the subject of several reports in the literature. These interactions may involve ionic attractions, Van der Waals' forces or hydrogen bond formation. Ionic forces are usually involved when the ionised form or organic acids and bases are sorbed by polamides by interaction with the amino and carboxylic end-groups in the polymer (Myagkov, 1956). Iijima and Sekeido (1962) have postulated that acidic dyes such as orange I could interact with the polyamide by both ionic and hydrogen bond formation. Berg and coworkers (1965) suggested that the uptake of organic acids such as formic acid only involves forces of the Van der Waals' type, a mechanism which has also been attributed to the interaction of chlorbutol with nylon 6:6 (Berg et al 1965).

Kapadia and his colleagues investigated the interaction of a number

of 4-hydroxybenzoate derivatives and proposed that these solutes formed very weak hydrogen bonds with the amide groups in the polymer which were then stabilised by Van der Waals' forces (Kapadia 1964). Later work by Richardson (1973) proposed that the sorption of ethyl 4-aminobenzoate by nylons may also be related to the swelling of the matrix by water.

The internal structure of the nylon 6 matrix consists of regions of amorphous and crystalline structural arrangement in which the extent of hydrogen bonding is small and great, respectively. Hydration of the amorphous areas of the matrix occurs by the formation of tightly bound loosely bound and capillary condensed water (Puffr and Sebenda 1967). Furthermore, chemically, the matrix consists of polar and non-polar regions which correspond to the local relative abundance of amide groups and methylene chains. These are therefore three possible mechanisms of binding which arise from these considerations.

1. A solute, unable to form hydrogen bonds directly with the polymer, may associate with the hydrophobic regions present by the formation of weak Van der Waals' forces.
2. Solute molecules which are capable of forming weak hydrogen bonds with the polymer, but are unable to displace bound water from the amide linkages, may form an association with this bound water. In this case sorption of the solute would depend upon the degree of hydration of the matrix.
3. Direct association of a solute with the polyamide can arise in two ways. A solute capable of forming moderately strong hydrogen bonds could displace loosely and tightly bound water from the amide groups in the amorphous regions of the matrix

and hydrogen bond directly. A strong interaction would be favoured in this case. If, however, the solute was not capable of forming sufficiently strong hydrogen bonds to break the interchain hydrogen bonds in the polymer, access to highly crystalline regions would not occur and sorption would probably cease with the presence of a plateau in the isotherm. Access to the crystalline regions, due to the ability of the solute to break interchain hydrogen bonds in these areas of the matrix would result in eventual plasticization and dissolution of the polymer.

The sorption and desorption isotherms for a weak organic electrolyte such as ethyl 4-aminobenzoate by nylon 6 powder have been shown previously to be not significantly different (Richardson 1973). The sorption and desorption isotherms for phenol and 4-nitrophenol are also not significantly different (table 3.13). This would indicate that the sorption process is reversible and does not involve chemisorption.

A close correlation between sorption and the percentage of the solute in the unionised form has been found by Richardson (1973) and Ho (1977). This is reflected in the data obtained in this study for the sorption of ethyl 4-aminobenzoate from single and binary solute solution. The changes in the sorption K value and ionisation are shown in table 4.1 where it can be seen that the extent of sorption changes in response to the state of ionisation. As the concentration of species in the unionised form increases, sorption decreases suggesting that ionic interactions are not occurring. The pka value

Table 4.1 The Effect of pH on the Sorption on to Nylon 6 and Ionisation of Ethyl 4-aminobenzoate and 4-methoxybenzoic Acid.

Solute	pH	K $1\ Kg^{-1}$	Percentage Change	Percentage Unionised Solute	Percentage Change
ethly 4-aminobenzoate	3.44	21.8	57.3	88	59.1
	2.32	9.3		36	
4-methoxybenzoic acid	3.44	28.1	3.8	92	7.1
	2.32	29.2		99	

for ethyl 4-aminobenzoate was obtained at 30° and an ionic strength of 0.5M (pka = 2.57; Richardson (1973), that for 4-methoxybenzoic acid was not corrected for temperature and ionic strength, (pka = 4.47 ; Albert and Sergeant 1971). The application of this uncorrected pka value may account for the lower degree of coincidence for the 4-methoxybenzoic acid percentage change values for sorption and the percentage of species in the unionised form. The pH dependence of the K value cannot be regarded as direct evidence of hydrogen bond formation between solute and polymer as it has been shown that the sorption of alkyl 4-hydroxybenzoate derivatives by polyethylene, a non-polar polymer, is also at a maximum when the solute is fully unionised in the liquid phase. An approximately inverse linear relationship has been shown to exist between the $\log_{10}K$ value on the nylon 6 sorbent and the $\log_{10}$ solubility for structurally related compounds including 4-substituted benzoic acids and their ethyl esters (Richardson 1973), and substituted acetanilides (Ward and Upchurch, 1965). This suggests that the mechanism of the interaction between the solute and polymer is similar within the given series. From table 4.2, it is seen that although the solubility of 4-nitrophenol and phenol is 10-100 times greater than for ethyl 4-aminobenzoate and 4-methoxybenzoic acid at pH 2.32, the K values are of the same order of magnitude. This suggests there is a different interaction mechanism between nylon 6 and the two phenols from that between the polymer and ethyl 4-aminobenzoate and 4-methoxybenzoic acid. Studies on the solubility dependence of the sorption process have shown that the 4-hydroxy derivative of a series of 4-substituted benzoic acid derivatives has a much higher affinity for nylon 6 than would be predicted from

solubility considerations (Richardson, 1973).

The solubility and K values can be related to one another using the following rectilinear relationship :

$$\log K = -0.33 \log_{10} S + 0.446 \quad \ldots\ldots\ldots\ldots (4.6)$$

where K = the sorption constant

S = aqueous solubility

which was found to be valid for the series 4 - Br, - NO_2, - OCH_3, - $COCH_3$, - CN , - F benzoic acids. Table 4.3 shows the observed and predicted K values for the model solutes using equation 4.6. It can be seen that ethyl 4-aminobenzoate and 4-methoxybenzoic are reasonably close to the predicted values, however, the phenolic derivatives appear to have a significantly higher affinity. This together with the observation that phenol is a solvent for nylon 6 suggests that phenol and 4-nitrophenol may be able to form specific hydrogen bonds with the amide groups of nylon 6.

Table 4.2 Affinity Constant, K, for the Sorption of Model Solutes by Nylon 6 Powder and Solubility at 30°.

pH	Solute	K (lkg^{-1})	Standard Deviation	Solubility at 30° (M)
2.32	ethyl 4-amino-benzoate	9.3	0.2	1.05×10^{-2} a
	4-methoxybenzoic acid	29.2	0.3	1.50×10^{-3} b
	4-nitrophenol	42.3	0.9	1.39×10^{-1} c
	phenol	11.6	0.3	7.84×10^{-1} c
3.44	ethyl 4-amino-benzoate	22.3	0.6	7.40×10^{-3} c
	4-methoxybenzoic acid	28.1	0.8	1.63×10^{-3} c

a Solubility data obtained by calculation from data of Richardson and Meakin (1974).

b Literature value for unionised 4-methoxybenzoic acid at pH 1.0 (ionic strength 0.5M) (Richardson 1973).

c Experimentally determined.

The influence of temperature on the sorption of the model solutes further emphasises the difference in the interaction mechanism. The extent of sorption generally decreases as temperature rises which corresponds to a weakening of solute-sorbent bonding and increased solubility of the solute in the liquid solvent phase. The sorption of all four model solutes from single solute solutions demonstrates this general trend (figures 3.13 and 3.17)

Table 4.3 Observed and Predicted Values of K for the Sorption of the Model Solutes on to Nylon 6 using the Solubility Relationship given in Equation 4.6.

Solute	Solubility * (M)	Observed * K value 1 Kg^{-1}	Predicted K value 1 Kg^{-1}
4-nitrophenol	0.139	42.3	5.4
phenol	0.784	11.6	3.0
ethyl 4-amino-benzoate	1.05×10^{-2}	9.3	14.1
4-methoxybenzoic acid	1.50×10^{-3}	29.2	23.2

* pH 2.32 (ionic strength 0.5M); 30^{o}

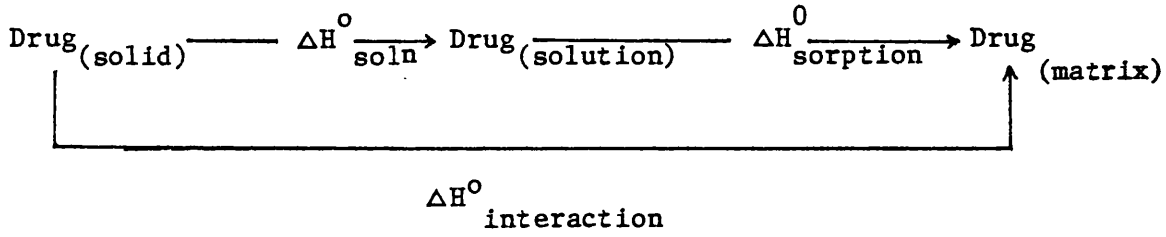
The sorption of ethyl 4-aminobenzoate and 4-methoxybenzoic acid showed a change in the slope of the Van't Hoff isochore at about 40^{o} (figure 3.13). Discontinuities have been reported previously for the sorption of ethyl 4-aminobenzoate from a 0.5M potassium chloride solution by nylon 6 powder (Richardson, 1973) and the permeation of water (Mosicek 1976) and ethyl 4-aminobenzoate through nylon films (Ho, 1977). The changes in slope of the Van't Hoff isochores reflect a lower solute affinity above 40^{o} than would be predicted

from an extrapolation of the isochore determined below 40°. This suggests that the sorption process is changing in nature possibly due to regions of the polymer matrix becoming impenetrable to the solute molecules. Ho (1977) has attributed this behaviour to thermally induced phase transitions in the polymer affecting the nature of the sorption interaction. The extent of hydrogen bonding within the matrix itself is increased as the polymer is heated above 45° and this effect has been demonstrated to influence the sorption of ethyl 4-aminobenzoate in nylons 6, 11 and 12 (Ho 1977).

The Van't Hoff isochores for phenol and 4-nitrophenol do not show the point of inflexion characteristic of the benzoic acid derivative sorption systems, and are linear over the temperature range studied (figure 3.17). This may be due to the phenolic compounds plasticizing the polymer resulting in a shifting of the transition inflexion to a much lower temperature (Roff 1971). This could be explained by the ability of phenolic compounds to form strong hydrogen bonds with the polymer, thus interfering with the consolidation of inter and intrachain hydrogen bonds which occurs at the temperature of the secondary phase transition. The lack of a discontinuity in the isochore for the sorption of ethyl 4-amino-benzoate by nylon 6 powder from ethanol was attributed to the ability of the solvent to plasticize the nylon matrix (Richardson 1973).

Enthalpies of sorption, ΔH^{o} sorption, for the interaction of various solutes have been commonly used for comparative purposes in an attempt to assign the type of binding mechanism operating to bring about the sorption of solutes. The values of ΔH^{o} sorption obtained for various solutes are summarised in table 4.4. The values obtained

for the model solutes in this study are also included for comparison. Consideration of the literature ΔH^{o} sorption values and the proposed mechanisms shows that there is no clear numerical trend to distinguish between phenolic solutes thought to form hydrogen bonds and other solutes considered to bind less strongly. The ΔH^{o} sorption values obtained in this study are similar in order of magnitude to those in the literature. It is therefore likely that the ΔH^{o} sorption values cannot be used as a basis for differentiating between sorption mechanisms. Effective determination of the enthalpy associated with the solute-polymer interaction from sorption experiments requires separation of the solute dissolution effects from those of the overall sorption process. One such method is based on the Hess relationship outlined in the energy balance diagram below (Richardson, 1973).



If the standard state is taken to be unit molality for the solution : polymer equilibria and unit mole fraction for the solid-solution phase equilibria, the ΔH^{o} interaction can be calculated from the slopes of the Van't Hoff isochores for the two processes (equation 4.7).

$$\Delta H^{o}_{interaction} = \Delta H^{o}_{sorption} + \Delta H^{o}_{dissolution} \quad ...(4.7)$$

Table 4 4 The Standard Enthalpy Change and Proposed Mechanism for the Interaction of Various Model Solutes and Nylon Polymers

Solute	Polyamide Type	$\Delta H^{o}_{Sorption}$ KJ mol^{-1}	Proposed Mechanism	Reference
LITERATURE				
formic-butyic acid	6 6	-0.2 - -2.9	Van der Waals forces	Berg et al(1965)
chlorbutanol	6:6	-4.6	Van der Waals forces	Berg et al(1965)
4-OH benzoates	6:6	-10.9 to -13.8	Hydrogen bonds Van der Waals forces	Kapadia et al(1964)
sorbic acid	6:6	-41.8	Hydrogen bonds	Rodell et al(1964)
phenol	not reported	-19.0	Hydrogen bonds	Chipalkatti(et al(1954)
benzoic acid	6:6	-9.0	Van der Waals forces	Browne et al(1956)
ethyl 4-aminobenzoate	6	-9.9	Hydrogen bonds + Van der Waals forces	Richardson (1973)

Table 4 4 Continued

Solute	Polyamide Type	$\Delta H^{o}_{Sorption}$ KJ mol^{-1}	Proposed Mechanism	Reference
THIS WORK - FROM SINGLE SOLUTE SORPTION STUDIES				
ethyl 4-aminobenzoate	6	-4.4 a -11.0 b	Van der Waals	
4-methoxybenzoic acid	6	-11.9 a -20.1 b	Van der Waals	
phenol	6	-5.7	Hydrogen bond	
4-nitrophenol	6	-14.1	Hydrogen bond	

a) $5^{o} - 40^{o}$ b) $40^{o} - 60^{o}$

For dilute solutions the ΔH^{o} values are proportional, therefore summation can take place although the standard states are not consistent. It is not possible to calculate the ΔG^{o} and ΔS^{o} for the interaction process, however, because the standard states are not the same and because of the nature of the system. It is not possible to use the mole fraction standard state for the calculation of the thermodynamic parameters associated with the sorption process, nor is it possible to use the molal standard state for the dissolution system. The $\Delta H^{o}_{interaction}$ values for the model solutes are summarised in Table 4.5.

Table 4.5 $\Delta H^{o}_{INTERACTION}$ Values for the Model Solute - Nylon 6 Interaction.

Solute	$\Delta H^{o}_{INTERACTION}$* $KJ\ mol^{-1}$	Standard Deviation
phenol	+ 0.1	0.8
4-nitrophenol	+ 14.1	2.3
ethyl 4-aminobenzoate	+ 30.8 ** - 24.2 ***	1.6 1.5
4-methoxybenzoic acid	+ 15.2 ** 7.0 ***	1.2 2.7

* Single solute values

** $5^{o} - 40^{o}$

*** $40^{o} - 60^{o}$

The $\Delta H^{o}_{interaction}$ data indicate that there may be an energetic basis for differentiating between the difference in behaviour of the phenolic and benzoic acid derivatives. The $\Delta H^{o}_{interaction}$ is representative of an imaginary process where the solid solute, in its standard state, is effectively "dissolved" in the polymer matrix. The $\Delta H^{o}_{interaction}$ values are, therefore, an approximate measure of the energy associated with the interaction between the matrix and the solute molecules. It is apparent that less heat is required to "dissolve" phenol in the nylon matrix than the other four solutes. It is possible therefore that a strong hydrogen bond can form with virtually no overall enthalpy change. This is not the case, however, when weak hydrogen bonding solutes interact. The value of + 14.1 KJ mol^{-1} for the $\Delta H^{o}_{interaction}$ of 4-nitrophenol is more difficult to explain. This solute behaves like phenol when the nature of the Van't Hoff isochore is considered but the enthalpy of interaction suggests that its behaviour, in this case, is more like that of the two benzoic acid derivatives. A possible explanation is that 4-nitrophenol may bind by a dual mechanism which involves both the hydroxyl and the nitro group. It is apparent from the $\Delta H^{o}_{interaction}$ of phenol that hydrogen bond formation does not give rise to a finite enthalpy change. It is, therefore, possible that the $\Delta H^{o}_{interaction}$ of +14.1 KJ mol^{-1} is due to a secondary weaker binding mechanism. A dual binding mechanism would also be consistent with the unusually high K value for the sorption of 4-nitrophenol.

4.1.2.1.2 The Dynamic Sorption of the Model Solutes in Nylon 6.

The determination of parameters associated with the rate of

mass transfer in nylon 6 is of fundamental importance to the overall characterisation of the sorption interaction. It was also necessary to study the rate of mass transfer within nylon 6 film to aid the interpretation of the sorption of solutes on to nylon 6 coated active carbon (Section 3.5). As the interaction of phenol with nylon 6 coated active carbon was not studied, it was not included in the assessment of film permeability. It has been shown previously that the sorption of solutes on to nylon 6 powder proceeds at a high rate with equilibrium being achieved within approximately 30 seconds at room temperature (Richardson 1973). Film permeability experiments have been used to study the mass transfer characteristics of nylon 6 with respect to ethyl 4-amino-benzoate (Ho 1977), and this method was selected to determine the sorption characteristics of the nylon 6 - model solute systems used here. The diffusion coefficient was determined from the Barrer plots for the rate of appearance of solute in the receptor compartment of the permeability apparatus (Figure 3.67) using the lag-time method (Section 1.6.1.1). The permeability coefficient was also calculated from the steady-state regions of the Barrer plots which establishes the rank order of permeability as (Table 3.49):

4-nitrophenol > 4-methoxybenzoic acid > ethyl 4-aminobenzoate

The diffusion coefficients, also shown in table 3.49 indicate that the diffusion coefficients of all three solutes are not significantly different at 30^{o}. If this is the case and equation 1.24 applies, the difference in permeability can be accounted for by differences in the sorption constants.

$$P = K \times \bar{D} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.24)$$

where P = Permeability coefficient

K = Sorption Constant

$\bar{D}$ = Diffusion Coefficient

This can be tested by calculating P from equation 1.24 and comparing it to the value obtained directly from the Barrer plot.

Table 4.6 Comparison of Permeability Coefficients Obtained Using Equation 1.24 and from the Barrer Plot.

Solute	$\bar{D}$ $\times 10^{13} M^2 sec^{-1}$	K* lkg^{-1}	$P \times 10^{12} m^2\ sec^{-1}$	
			Equation 1.24	Barrer Plot
4-nitrophenol	1.09	42.3	4.61	4.95
4-methoxybenzoic acid	0.90	29.2	2.63	3.57
ethyl 4-amino-benzoate	0.86	9.9	0.85	0.77

* nylon 6 powder

The permeability values calculated by the two methods appear to agree reasonably closely, the percentage differences between the P values being 25%, 8% and 2% for 4-methoxybenzoic acid, 4-nitrophenol and ethyl 4-aminobenzoate respectively. Previous studies have shown that differences exist between the K values for nylon 6 film and powder which have attributed to differences in crystallinity (Richardson 1973). This could account for the discrepancy between the P values determined by the two methods. It would appear therefore that the overall permeability may be predicted from the product of the diffusion coefficient and K values and that any relative change in permeability arises from the differences in the K value.

4.1.2.2 ACTIVE CARBON.

4.1.2.2.1 The Equilibrium Sorption of the Model Solutes by Active Carbon.

The general procedure used to obtain isotherm data was shown to be satisfactorily reproducible although the variability of the data appeared to be generally higher relative to the isotherms obtained for sorption on to nylon 6 powder. It is likely that this variability arises from the overall non-uniformity of the granules within a given batch of active carbon resulting from the natural origin of the material. Several workers have recognised this problem and have milled their samples to enhance the degree of uniformity (Radke and Prausnitz 1972b, Jossens et al 1978). It has been shown, however, that the milling process increases the specific surface area of the sorbent (Weber and Morris 1963), and would thus not allow comparison with the nylon 6 coated granules.

The isotherms for all the solutes were non-linear and of the L type according to Giles' classification. The isotherms for phenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate were L_1 type in nature whereas that for 4-nitrophenol was of L_2 type which is characterised by the presence of a plateau (Figures 3.22 - 3.25).

The affinity of the model solutes for the active carbon was higher than for the nylon 6 sorption systems although the rate of attainment of equilibrium was much lower. The high capacity of the adsorbent was therefore only apparent after approximately three days using shake-flask experimental conditions. The non-linear nature of the isotherms does not allow their characterisation by a single sorption constant as with the nylon 6 sorption isotherms. Several mathematical models have been developed to describe non-linear

isotherms which have been outlined in Section 1.5.2.1. In order to be able to compare the interactions of the model solutes with active carbon the models used should ideally meet the following criteria :

1. The model should fit all types of L isotherm.
   The constants that characterise the isotherm should be able to be determined independently of the concentration range studied.
2. The constants should numerically represent physically important features of the interaction which, in the case of active carbon would be the affinity and capacity for a given solute.

Three models were evaluated for their ability to describe the non-linear isotherm data obtained in this study; the Langmuir, Freundlich and Radke equations (3.8, 3.9 and 3.10 respectively). Constants for the Langmuir and Freundlich equations were determined by subjecting the data to a computerised linear regression analysis according to the rearranged forms given below:

Langmuir : $$\frac{1}{n} = \frac{1}{n_{max}.b.C_{eq}} + \frac{1}{n_{max}} \quad \text{.....(4.8)}$$

Freundlich: $$\log_n = \log a + \frac{1}{m} \log C_{eq} \quad \text{.....(4.9)}$$

The isotherm constants were also determined using a non-linear regression program, NONLIN (Metzler et al 1974) which is based on a modified Newton iteration technique. The program is supplied with estimates of the isotherm constants and the model equation together with the experimental data. The program improves the estimates of the isotherm constants, using the principle of

minimising the difference of the sum of squared deviations between the experimental and best-fit isotherm profile data. The final value of the sum of squared deviations can be used to determine the degree of fit achieved using a particular isotherm model. The sum of squared deviations is defined in equation 4.10.

$$SSD = \sum_{N} (n_{exp} - n_{calc})^2 \quad \ldots\ldots\ldots\ldots (4.10)$$

where n_{exp} = the experimental uptake

n_{calc} = the value of uptake calculated from the isotherm equation using constants obtained from regression analysis

N = the number of experimental data points

SSD = the sum of squared deviations

The sum of squared deviations for the Freundlich and Langmuir equations are given in table 4.10 using both regression techniques. The table also includes constants for the Radke equation which is an intrinsically non-linear function and therefore cannot be rearranged to give a linear relationship from which the constants may be determined.

Table 4.4 shows that the constants obtained using different regression methods yield different values for the sum of squared deviations. This probably arises from the effect of the rearrangement process on the error associated with the experimental data points. Figures 4.1 and 4.2 show the data plotted according to equations 4.8 and 4.9 respectively where it can be seen that the weighting of the points changes after rearrangement due to a spatial redistribution of the data. In both cases data in the low concentration region is given a high weight and a small degree of error associated with these data points will give rise to large changes in the values of the isotherm

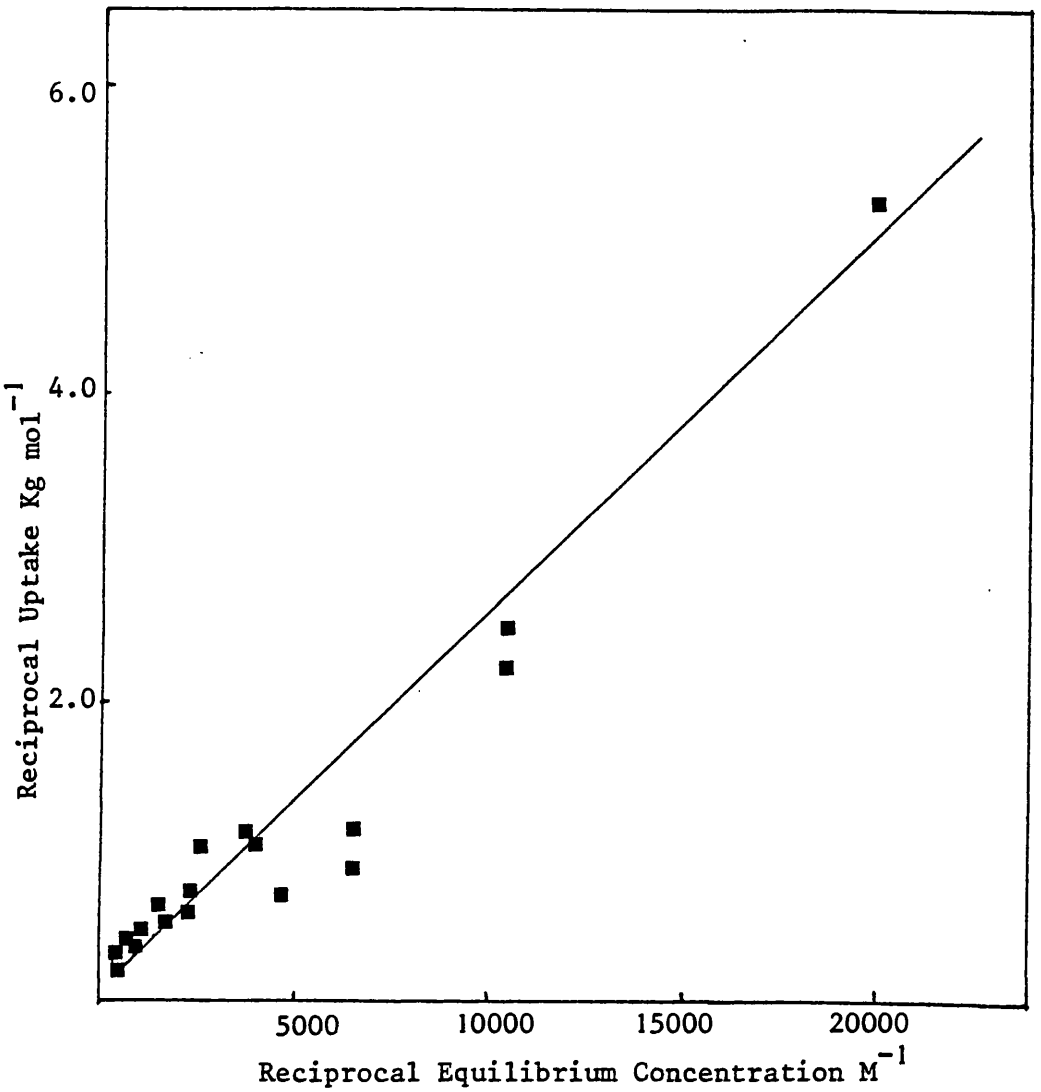


Fig 4.1: Data for the Isotherm for the Sorption of 4-nitrophenol by Active Carbon at pH 2.32 (0.5M Ionic Strength) and 30°, Plotted According to Equation 4.5.

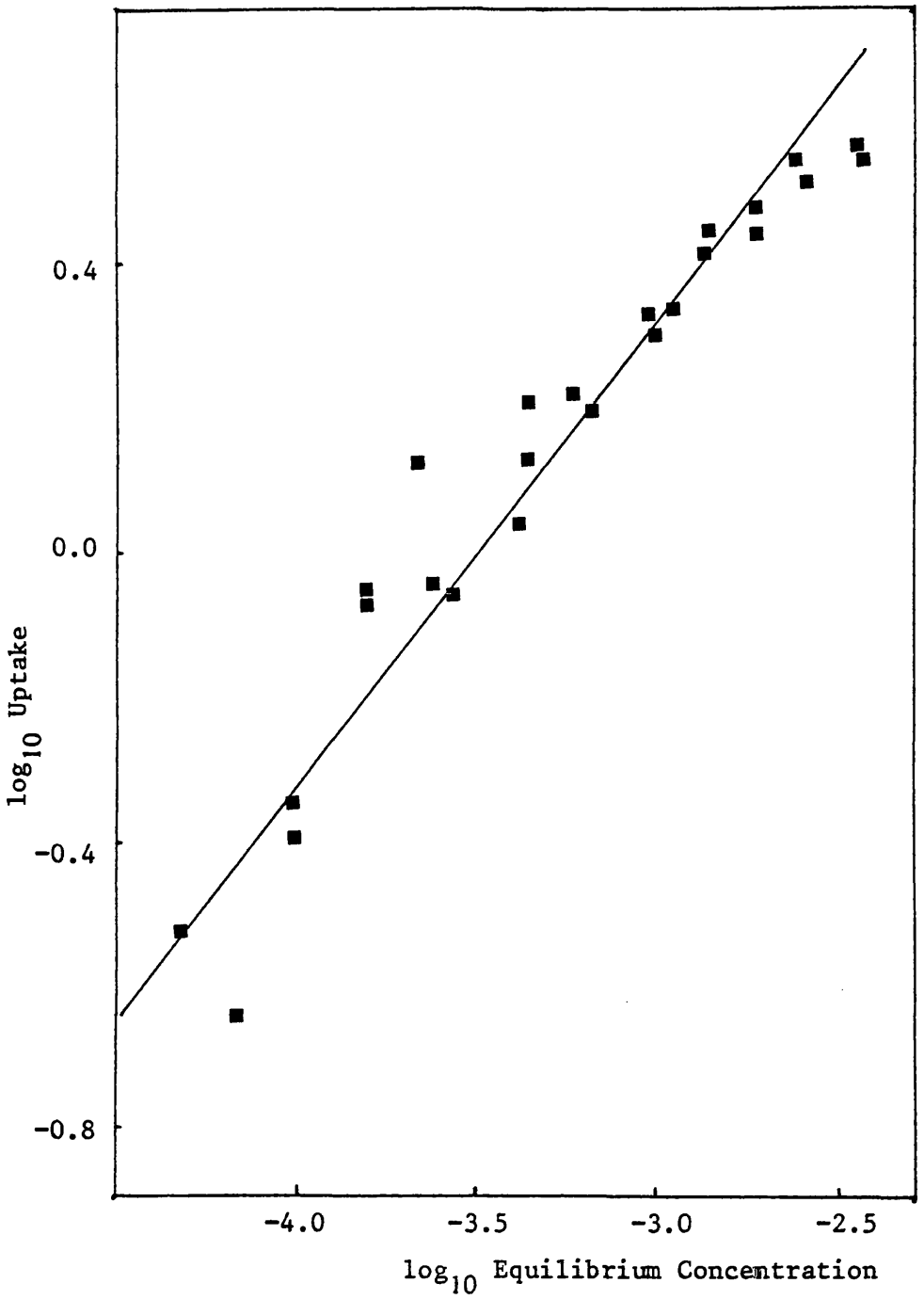


Fig 4.2 Data for the Isotherm for the Sorption of 4-nitrophenol by Active Carbon at pH 2.32 (0.5M Ionic Strength) Plotted According to Equation 4.6.

Table 4.10 The Sum of Squared Deviations for the Fit of Single Solute Sorption Data to the Langmuir Freundlich and Radke Equations.

Solute	Isotherm Type	FREUNDLICH		LANGMUIR		RADKE
		RLR[1]	NLR[2]	RLR	NLR	NLR
4-methoxybenzoic acid	L_1	0.38	0.35	0.70	0.56	0.56
4-nitophenol	L_1	2.19	1.20	1.43	1.19	0.98
	L_2^1	37.42	8.75	26.46	1.20	1.19
ethyl 4-aminobenzoate	L_1	1.26	0.67	21.13	1.15	0.59
phenol	L_1	0.14	0.09	0.13	0.10	0.10

1. Rearrangement and linear regression.

2. Non-linear regression.

constants. The Everett plot was also tested which is a derivative of equation 4.8 obtained by multiplying throughout by C_{eq} (Everett 1964). While this plot improved the spatial arrangement of the data restoring the original spacing of points, the fit was not significantly different from the plot of equation 4.8 as determined by the numerical value of the sorption constants. It would appear, therefore, that transformation of the data results in the low degree of fit. The use of data without prior rearrangement may therefore be preferable with respect to the first criterion of "goodness of fit"; the sum of squared deviations can be used to determine how close the fit is to the experimental data. The regression technique which gives the lowest value of the sum of squared deviations will produce the most accurate estimates of the isotherm constants for a given model. Similarly, the isotherm model which gives rise to the lowest value of the sum of squared deviations is the most accurate representation of the isotherm data. Table 4.4 shows that the isotherm for the 4-methoxybenzoic acid and phenol equilibria are fitted closely by all three models. The L_1 isotherm of ethyl 4-aminobenzoate is successfully described by the Freundlich and Radke equations but less well by Langmuir's equation. The difference in the sum of squared deviations between the linear and non-linear regression lines is clearly illustrated for the determination of the Langmuir isotherm constants. The Freundlich equation successfully predicts L_1 type behaviour in all cases as would be expected from a consideration of the similarity between the functional form of the equation and the general shape of the L_1 isotherm. The Freundlich equation does not however describe the L_2 type behaviour of 4-nitrophenol which is characterised by the

presence of the plateau, again as would be expected from consideration of the nature of the equation. Although the Freundlich equation fits the experimental isotherm data of 4-methoxybenzoic acid and phenol more closely, the Radke equation appears to be the most widely applicable model as the sum of squared deviations is low for both L_1 and L_2 type isotherms.

Table 4.7 indicates that the Freundlich and Langmuir equations do not comprehensively describe L_2 and L_1 data for 4-nitrophenol respectively, however, the Radke equation does.

The second criteria proposes that the constants from the various isotherm equations should numerically represent some aspect of the interaction, thus enabling a quantative comparison of the sorption of the four model solute equilibria. Although the Freundlich equation fits L_1 type isotherm data satisfactorily, the equation is empirical and as such the constants have no specific physical meaning.

The Langmuir equation constants are derived from a consideration of the Langmuir surface model where the b' constant is a function of solute affinity and the n_{max} term, the capacity of the sorbent for a given solute. As all four model solute molecules are of approximately the same size, the values of n_{max} would be expected to be similar. In all cases the values of n_{max} determined were reasonably consistant ranging from 3.66 mol kg^{-1} for phenol to 4.62 mol Kg^{-1} for 4-nitrophenol (data from the L_2 isotherm region). Comparison of isotherm data in the L_1 region by visual inspection (figure 3.22) reveals that the rank order of affinity of the four solutes for active carbon is as follows :

4-methoxybenzoic acid > 4-nitrophenol > ethyl 4-aminobenzoate > phenol

Although the Langmuir equation is capable of resolving the isotherms for the sorption of 4-methoxybenzoic acid and phenol, the rank order of affinity with respect to 4-nitrophenol and ethyl-4-aminobenzoate is reversed (figure 3.22 table 3.32). It would appear, therefore, that whilst the Langmuir b' constant can describe the order of affinity of widely different isotherms, it cannot resolve those which lie close to one another. It is also of interest to note that the constants for the Langmuir equation obtained for both the L_1 and L_2 isotherms of 4-nitrophenol are similar and thus apparently independent of the isotherm range over which they were determined (table 3.32). The other two isotherm models did not exhibit such behaviour.

The Radke equation consists of three constants whose relative values determine whether the equation adopts a form which approximates to the Langmuir and Freundlich equations (see Section 1.5.2.1). As the value of the constant γ approaches zero, the equation becomes Langmurian in nature and can be related to the Langmuir equation as follows :

$$\beta \cong n_{max} \quad ; \quad \text{when} \quad \gamma = 0 \quad \ldots\ldots\ldots\ldots (4.11)$$

$$\frac{\alpha}{\beta} \cong b' \quad ; \quad \text{when} \quad \gamma = 0 \quad \ldots\ldots\ldots\ldots (4.12).$$

Further consideration of the Radke equation reveals that a comparison with the Freundlich equation will also occur only for highly active carbons i.e. when the Henry's law constant α is large compared to the β constant and the γ constant is greater than zero. This can be seen by rewriting the Radke equation :

$$\frac{1}{n} = \frac{1}{\alpha c} + \frac{1}{\beta c^{\gamma}} \qquad \text{.....(4.13).}$$

then $n \simeq \beta^{\gamma}$; when $\alpha >>> \beta$ .....(4.14)

and $\gamma \neq 0$

Therefore when $\alpha >>> \beta$ and $\gamma \neq 0$

$$\beta \simeq a \qquad \text{.....(4.15)}$$

and $$\gamma \simeq 1/m \qquad \text{.....(4.16)}$$

Table 3 indicates that when fitted to the L_1 isotherm data, the Radke γ constant has a finite value between 0 and 0.5, suggesting that some degree of Freundlich behaviour is being shown.

That Radke γ constant together with the other constants can probably be used as an index of isotherm type with respect to Giles' classification. It is apparent from Tables 3.31 , 3.32 and 3.33 that although the isotherms for 4-methoxybenzoic acid and phenol appear to be L_1 in nature the Radke γ constant suggests that they tend more towards L_2 type behaviour. The L_1 type isotherms of 4-nitrophenol and ethyl 4-aminobenzoate have higher γ constants which would indicate that the isotherms are intermediate between L_1 ($\gamma \simeq 0$) and L_2 ($\gamma \simeq 0.5$) type. In accordance with equation 4.11 and 4.12 the Langmuir n_{max} and b constants for 4-methoxybenzoic acid agree well with the β constant and α/β constant ratio (Equation 4.11 and 4.12) of the Radke equation.

In conclusion, the Radke equation would appear to be the most generally applicable isotherm model with respect to this study as it can assume the mathematical features of both the Langmuir and Freundlich equations. In so doing the nature of the affinity and capacity terms remain and a further term is added which appears to be useful in characterising the overall nature of L type isotherm behaviour. Although the Freundlich and Langmuir isotherm equations

may be useful in fitting the special cases of L_1 and L_2 isotherms respectively, their general applicability appears to be limited. As the Radke α constant and the nylon 6 K value are both estimates of the Henry's law constant for adsorption (Radke and Prausnitz 1972a, Richardson 1973), the affinity of the solutes for active carbon and nylon 6 may be numerically compared.

4.1.2.2.2 The Dynamics of Sorption on to Active Carbon.

Preliminary studies of the equilibration time have shown that the sorption of the model solutes by active carbon is slow, taking approximately three days under conditions of low turbulence in the shake flask experiments. In many of the applications of sorbent materials such as the removal of potentially toxic materials from body fluids, the sorption rate is of great importance in assessing the efficiency of the sorbent. The overall dynamics of the sorption process may be subdivided into four possible rate controlling process as follows :

1. Solute transport in the bulk solution to the surface of the diffusion layer around the granules.
2. Film diffusion through the concentrated solute solution which forms at the solution-granule interface
3. Pore diffusion of the solute through the solvent filled pores to adsorption sites within the porous network
4. Adsorption from the solution present in the pore lumen to the site on the pore walls

To assess the factors influencing the extent to which the sorbent controls the rate of uptake, a fundamental study of rates of sorption was carried out under conditions of high agitation to minimise the effect of bulk solution transport and film diffusion on the kinetics

of sorption. At stirring speeds of 900 and 1000 rpm the kinetics of sorption of 4-nitrophenol were unchanged suggesting that rate limiting processes in the solution phase were eliminated and that the rate of sorption was being controlled by the porosity and sorption characteristics of the active carbon granules.

The kinetic profile obtained for a given solute was typically triphasic consisting of an initial region of rapid sorption of about 25 minutes duration, followed by a transitional region where the rate slowed, and a final steady state region (figure 3.44).

A possible explanation for the triphasic profile arises from a consideration of the distribution of mass within the sorbent granule as a function of time which is illustrated schematically in figure 4.3. When an active carbon granule comes into contact with the bulk solute solution a film of solute develops just within the granule in the peripheral region which will be referred to as the subspace. As solute diffuses into the subspace, it is adsorbed rapidly thus maintaining a steep concentration gradient between the bulk solution and the solution within the pore lumen which is the likely driving force for the sorption process. The subspace concentration arises because solute can enter this region from the solution faster than it can diffuse away towards the core of the granule. The subspace therefore effectively comes into equilibrium with the bulk phase solution a state which will be maintained as long as rapid sorption of solute continues. This region of the kinetic profile is described by the $t^{\frac{1}{2}}$ plot and relative rate constant (Section 1.6.2).

Having attained this preliminary steady-state, where the overall sorption rate is controlled by the relative rate of solute arrival into and departure from the subspace into the core, two factors

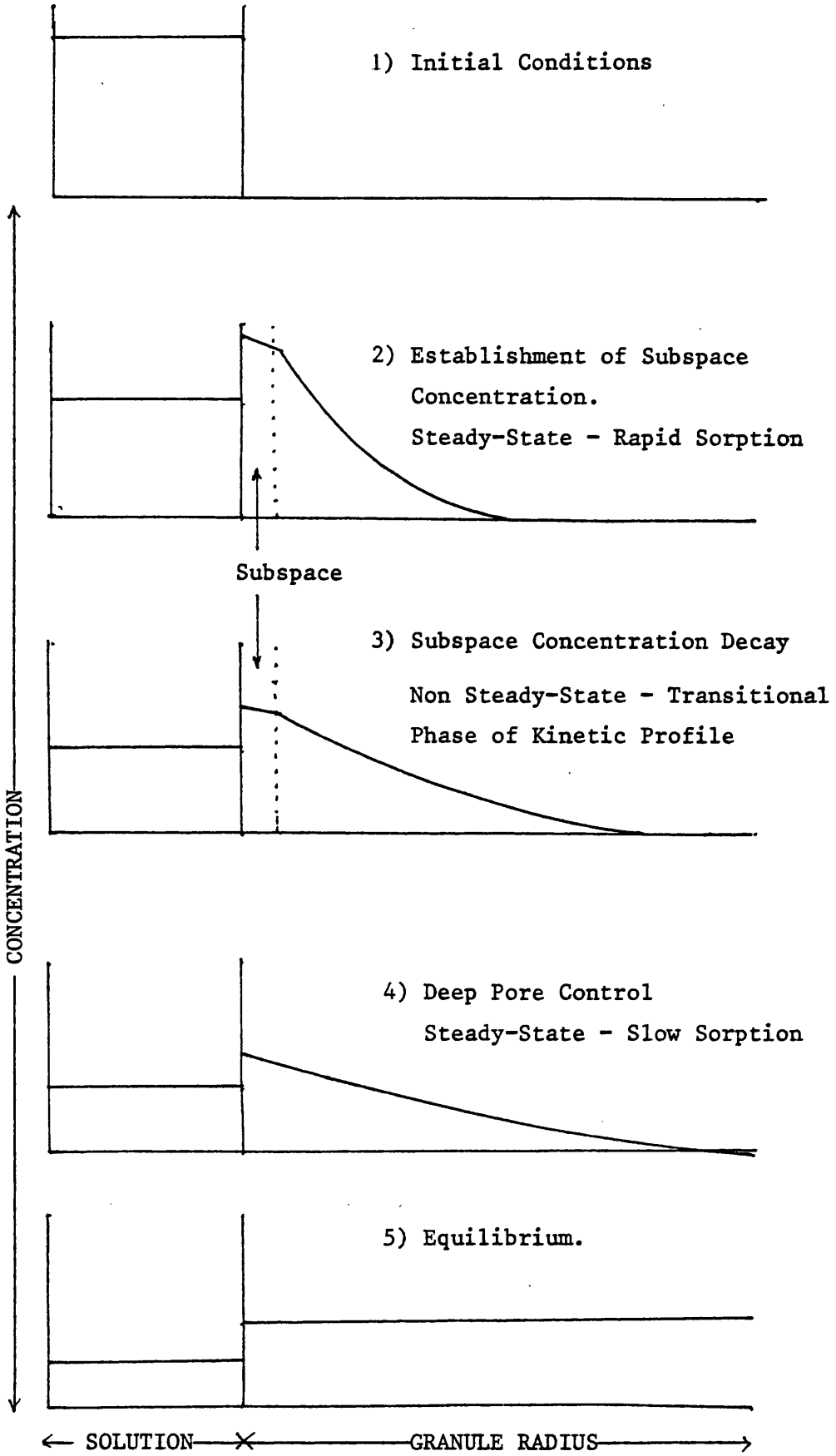


Fig 4.3 Schematic Representation of the Radial Distribution of Solute Within the Active Carbon Granule and Solution.

change which alter the nature of the system. The subspace concentration is maintained by the rate of solute arrival exceeding the rate of departure. As solute is removed from solution however, the subspace will acquire solute at a slower rate due to the lower solution-subspace concentration gradient. Secondly, as the concentration gradient across the radius of the granule diminishes due to solute accumulation, the differential concentration between the subspace and the core will also be reduced. As a result, the high subspace concentration decays to that of the granule core and the deep pore network assumes control of the rate of sorption until equilibrium is achieved. The adsorption process will therefore have a great influence on the overall rate of sorption. Throughout its radial diffusion into the core, solute is probably continually being adsorbed and desorbed until the distribution of solute adsorbed at equilibrium is constant at all points along the radial distance. This sorption-desorption process will also assist in maintaining a high concentration gradient between the solution in the granule pores containing solute free to diffuse within the granule and that in the bulk solution. It would be expected, therefore, that a higher rate of sorption would occur in more highly active carbons. Several factors which have been shown to affect the rate of sorption have been discussed in Section 1.6.2.1. To effectively quantify these effects, two approaches have been suggested in the literature. If the kinetic profile is replotted according to the square-root time relationship, a relative rate constant can be calculated from the slope of the linear portion of the curve (Weber and Morris 1963). Figure 3.45 shows that the initial linear period for the sorption of 4-nitrophenol extends over approximately 25 minutes

and appears to intercept the abscissa thus giving an apparent "lag-time" value. While the $t^{\frac{1}{2}}$ plot is a useful comparative parameter, Crank has suggested that mass transfer of solute into the carbon granule occurs under the control of a diffusion process. As such the rate of sorption should be a simple function of the concentration gradient between the solution and the granule core and the resistance to diffusion offered by its structural nature. Fick's second law should therefore be obeyed and the diffusion process responsible for determining the rate of disappearance of the solute from solution can be characterised by a single parameter, the diffusion coefficient (Equation 1.15). Due to the high activity of the carbon the adsorption component of mass transfer must be considered by modification of Fick's second law. This modification is referred to as the conservation of diffusing mass equation (Weber and Rumer 1965) as it introduces a sorption rate term (Equation 1.34).

$$\frac{dc_t^C}{dt} = \bar{D}.\frac{d}{dx}\left(\frac{dc_t^C}{dx}\right) - \frac{dM_t^C}{dt} \quad \text{.....(1.34)}$$

where c_t^C = the concentration of solute free to diffuse

t = time

$\bar{D}$ = the diffusion coefficient

M_t^C = uptake of solute i.e. that which is adsorbed and not free to diffuse

x = distance

Equation 1.34 divides the solute taken up into that free to diffuse and that which is immobilised due to adsorption. If correctly defined boundary conditions are used to solve equation 1.34 the rate at which solute is removed from solution will be a function of $\bar{D}$ and the two or more isotherm constants used to

express the adsorption component. In this respect the conservation of diffusing mass equation more correctly describes the nature of the interaction and should be used in preference to $t^{\frac{1}{2}}$ plot methods and the approximate method of Tien and Thodos (Crank : Personal Communication). Crank (1956) developed a method for solving equation 1.34 by the numerical analysis technique of solution by finite differences. This method was subsequently used by Weber and Rumer (1965) who published a computer program to enable simulation of kinetic profiles which could be used in conjunction with experimental data to obtain $\bar{D}$ by curve matching procedures. Crank was concerned with mass transfer in fibrous sorbents and although Weber and Rumer used granular active carbons they too utilised the model for the fibrous sorbent. The calculation of $\bar{D}$ in this study used the computer program of Weber and Rumer which was modified by replacing the finite difference approximations and boundary conditions for spherical rather than cylindrical diffusion media (Crank 1956). A full listing of this program is given in Appendix 4. The diffusion coefficient is calculated as follows : firstly the computer program is supplied with the initial conditions of the experimental conditions. These include

1. The volume of solution
2. The initial concentration of solute
3. The experimental sphere radius of the granules.
4. The number of granules in the system.
5. The two Langmuir equation constants.

The program is then supplied with the mathematical details for the solution which are :

1. The number of shells into which the granule is subdivided.
2. The accuracy required for each iteration step of the

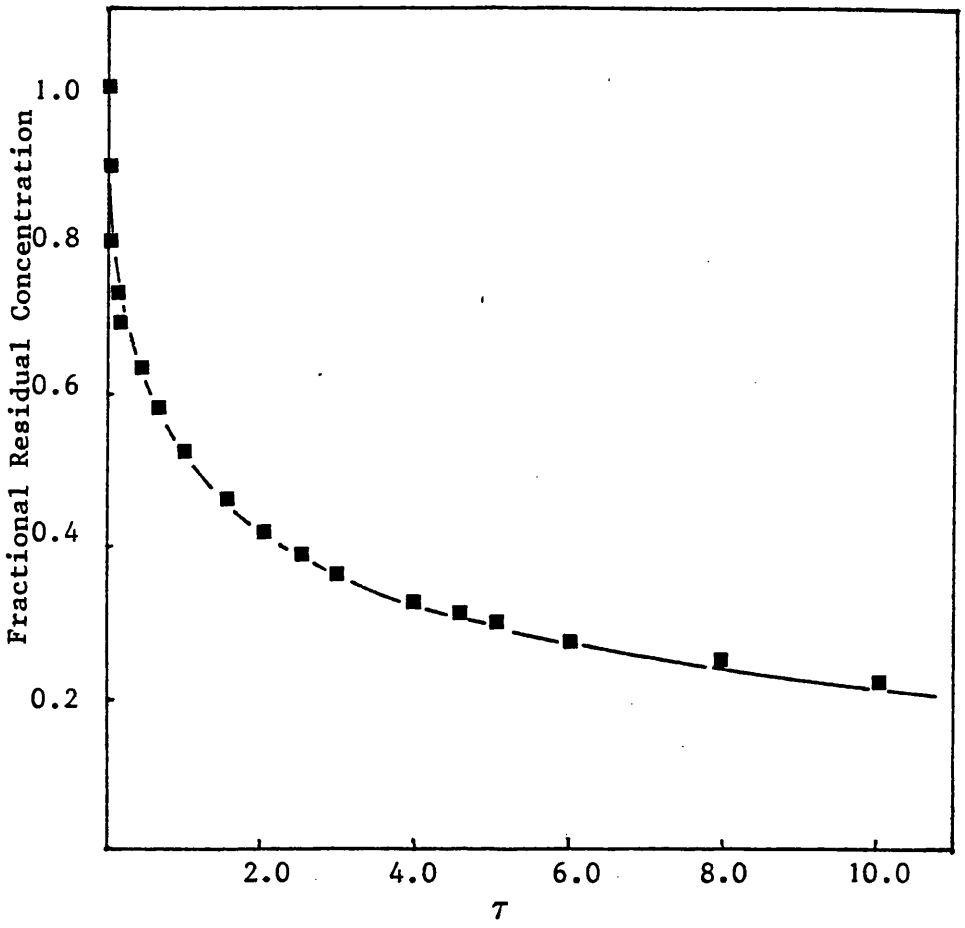


Fig 4.4: Simulated Curve for the Sorption of 4-nitrophenol by a Homogeneous Sphere with Identical Sorption Characteristics to Active Carbon from 1000ml of Solution; pH 2.32 (0.5M ionic strength).

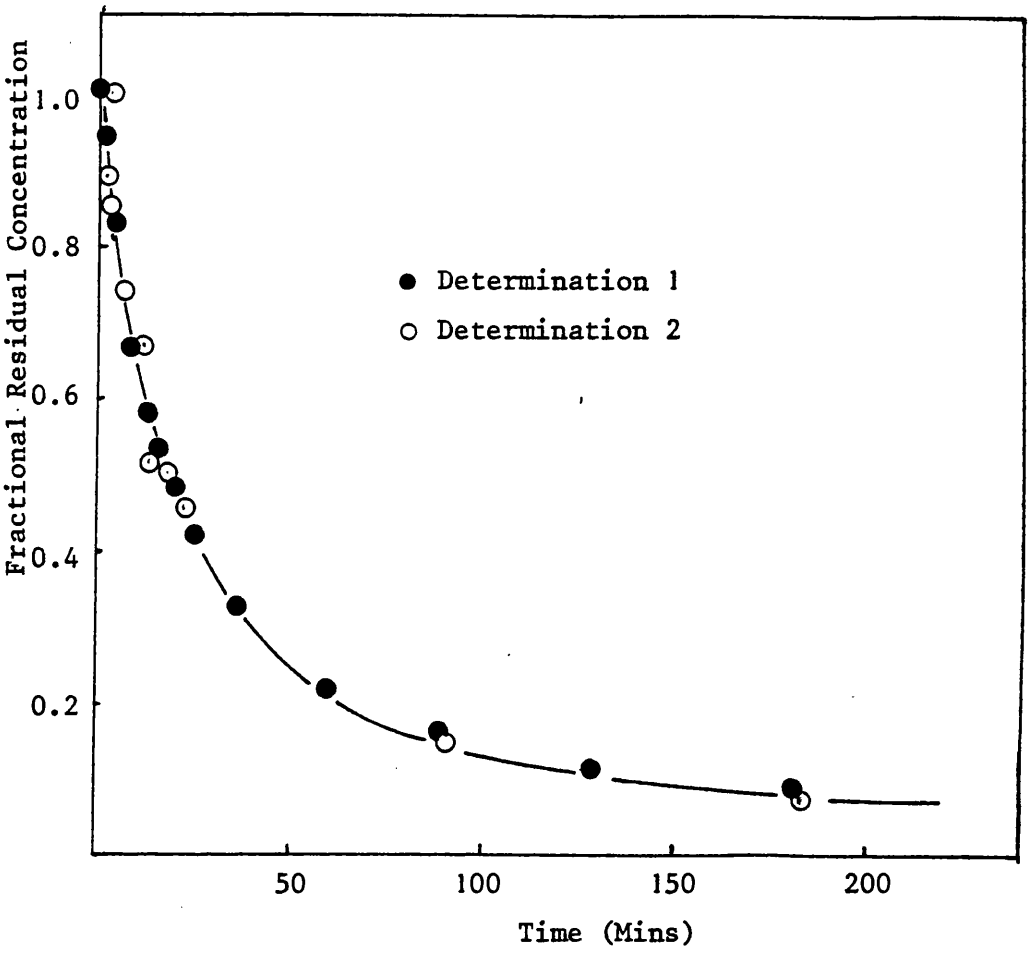


Fig 4.5: Data for the Sorption of 4-nitrophenol on to 2.0 gramme of Active Carbon from 1000ml of 10^{-3}M Solution; pH 2.32 (0.5M Ionic Strength) at 30^{o} Plotted as Fractional Residual Concentration vs Time.

calculation

3. The increments of τ , the dimensionless unit which represents advancing time.

The program output produces a plot of percentage residual concentration versus time increments of τ . The output for the simulation of the conditions of the experiment in which 4-nitrophenol is taken up by 2 gramme of active carbon at 30^{o} from 1000ml of a 10^{-3} M solution (pH 2.32; 0.5M ionic strength) is shown plotted in figure 4.4. The corresponding experimentally determined kinetic profile, also expressed as percentage residual concentration versus time, is shown in figure 4.5. If the initial conditions and the model are an accurate representation of the true situation the simulated profile and the experimental profile should be functionally related, differing only by an abscissa scale factor of $\bar{D}/a^{2}$. By matching the two curves, $\bar{D}$ can be calculated using equation (1.33)

$$\tau = \frac{\bar{D}}{a^{2}} \cdot t \quad \ldots\ldots\ldots\ldots \quad (1.33)$$

where $\bar{D}$ = diffusion coefficient

a^{2} = the granule equivalent sphere radius

τ = simulated time increments at given percentage residual concentration

t = experimental times at given percentage residual concentration.

Values of $\bar{D}$ were calculated in the initial and transitional rate regions of the kinetic profile by obtaining fifteen values and determining their mean and standard deviation. Figure 4.6 shows the relationship between τ and time for this 4-nitrophenol system. If the model simulated the kinetic situation exactly, the plot of t versus τ would be expected to be linear with a slope of $a^{2}/\bar{D}$.

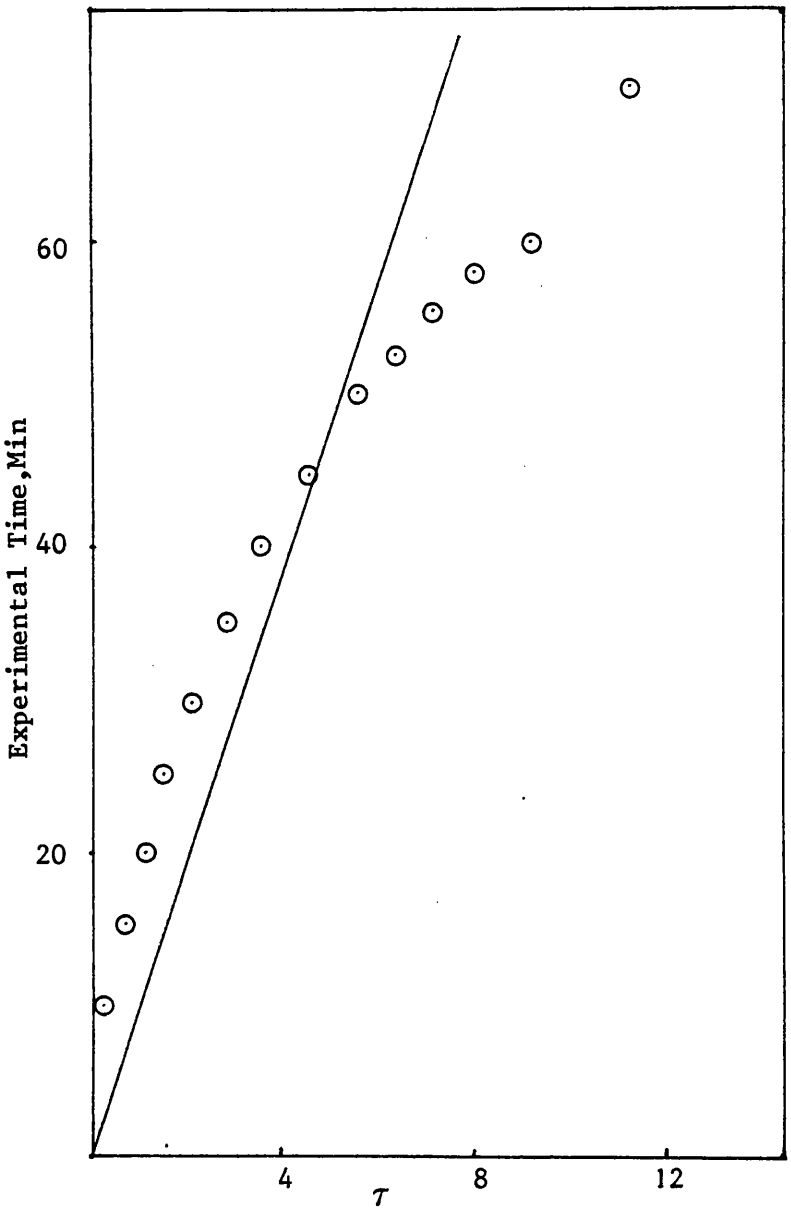


Fig 4.6: The Relationship between τ and Time for the Sorption Kinetics of 4-nitrophenol on to Active Carbon from 1000ml of a 10^{-3}M Solution at pH 2.32 (0.5M Ionic Strength) and 30^{o}

The plot in figure 4.6 is curvelinear over the initial 70 minute period suggesting that the system behaves non-ideally with respect to the conservation of diffusing mass equation (equation 1.34). This non-ideality can probably be accounted for by the heterogeneous nature of the diffusion medium arising from the different pore size ranges within the granule (Section 1.3.2). The solution to the conservation of diffusing mass equation assumes that the sorbent is a spherical, homogeneous diffusion medium whose adsorption characteristics are uniform throughout the structure. The calculation procedure utilises the Langmuir isotherm equation constants which are themselves subject to error. As the carbon is neither homogeneous with respect to both diffusion and adsorption due to the nature of the porous network, errors may arise because of this over simplification. The diffusion coefficient must, therefore, be regarded as an average diffusion coefficient which reflects the overall diffusion characteristics of the sorbent and which may not, in all cases necessarily be independent of conditions in the solute solution.

There are thus two methods by which factors influencing the overall rate of sorption may be assessed; the relative rate constant and the average diffusion coefficient. The relative rate constant has been shown to be influenced by experimental conditions whereas the average diffusion coefficient should be an invariant function of the sorbent's nature and therefore not influenced by environmental factors in the solution (Weber and Rumer 1965). The effect of granule weight and initial solute concentration have been shown to influence relative rate constant for sorption (Weber and Morris 1963) which has been confirmed by this study.

The kinetics of sorption of 4-nitrophenol was studied and the kinetic profile data was analysed in terms of the relative rate constant and the average diffusion coefficient. Table 3.35 shows that the relative rate constant increases as the granule weight in the solution is reduced. It is therefore apparent that although the absolute mass of solute removed is less, the percentage reduction of solute in solution is higher. The data from this aspect of the study is sparse but would indicate that the rate of uptake may be reaching a limiting value. Halving the granule weight increases the relative rate constant by a factor of 11%, however a further 25% reduction only gives rise to a 6% increase in the relative rate constant (Table 3.42). This suggests that the subspace within the granule may be becoming congested with solute as the granule weight is reduced and as the effective amount of solute increases with respect to each granule. If this congestion reaches a maximum value further decrease in granule weight will not result in an increase in the relative rate constant.

Table 3.36 shows that the relative rate constant increases, apparently asymtotically as the initial solute concentration is increased for a given sorbent weight. It is possible that this effect arises from subspace congestion resulting from increasing the effective amount of solute available to be adsorbed by the granule. As the solute concentration in solution is increased, the concentration gradient also increases resulting in a rapid rate of uptake with consequent congestion of the carbon subspace. It is, therefore, likely that increasing the amount of solute present in the system is equivalent to reducing the sorbent weight. These findings indicate that a consideration of the mass transfer

Table 4.8 Diffusion Coefficient Data for the Sorption of 4-nitrophenol from 1000ml of Solution at 30^{o} and pH 2.32 (0.5M ionic strength).

Initial Concentration $\times 10^{3}$ M	Sorbent Weight (gramme)	Average Diffusion Coefficient $\times 10^{9}$ M^{2} sec^{-1}	Standard Deviation $\times 10^{9}$	Coefficient of Variation %.
1.004	1.0	2.60	0.14	5.4
2.003		2.33	0.36	15.5
2.979		1.61	0.11	6.8
3.974		1.56	0.32	20.5
4.969		1.32	0.21	15.9
0.999	2.0	1.76	1.43	81.3
1.952		1.81	0.70	38.7
2.964		1.75	0.82	46.9
3.961		1.65	0.67	40.6
4.915		1.36	0.16	11.8
1.983	0.5	1.48	0.35	23.6

characteristics of the sorbent, in response to changes in the nature of the solution, may be more likely to yield useful information about the behaviour of the system than attempting to correlate changes in the nature of the sorption process with the physicochemical nature of the solution Average diffusion coefficients for the sorption kinetics of 4-nitrophenol in systems containing different amounts of carbon and initial solute concentrations are given in table 4 8 These data, shown in figure 4.7 indicate that, despite wide variations in experimental conditions, the average diffusion coefficient values are similar. The error in the determination appears to be greater at lower initial concentrations and higher granule weight which may reflect some degree of sensitivity to the physicochemical nature and dimensions of the sorption system.

These results differ from the relative rate constant data where a clear trend is observed with respect to initial solute concentration for both 1.0 gramme and 2.0 gramme granule weight systems (Figure 4.8). This may be explained by introducing the concept of solute permeability. If, as with polymeric sorption, the permeability through the carbon is the product of some function of the adsorption and diffusion process, then any representation of the overall kinetics of sorption would be influenced by factors affecting these two processes. For this reason, the kinetic profile, the $t^{\frac{1}{2}}$ plot and the relative rate constant are probably representative of gross solute permeability effects and as such will be sensitive to changes in the system which will influence the adsorption process. As the solution to equation 1.37 eliminates changes in experimental conditions by the use of carefully defined boundary conditions and utilises

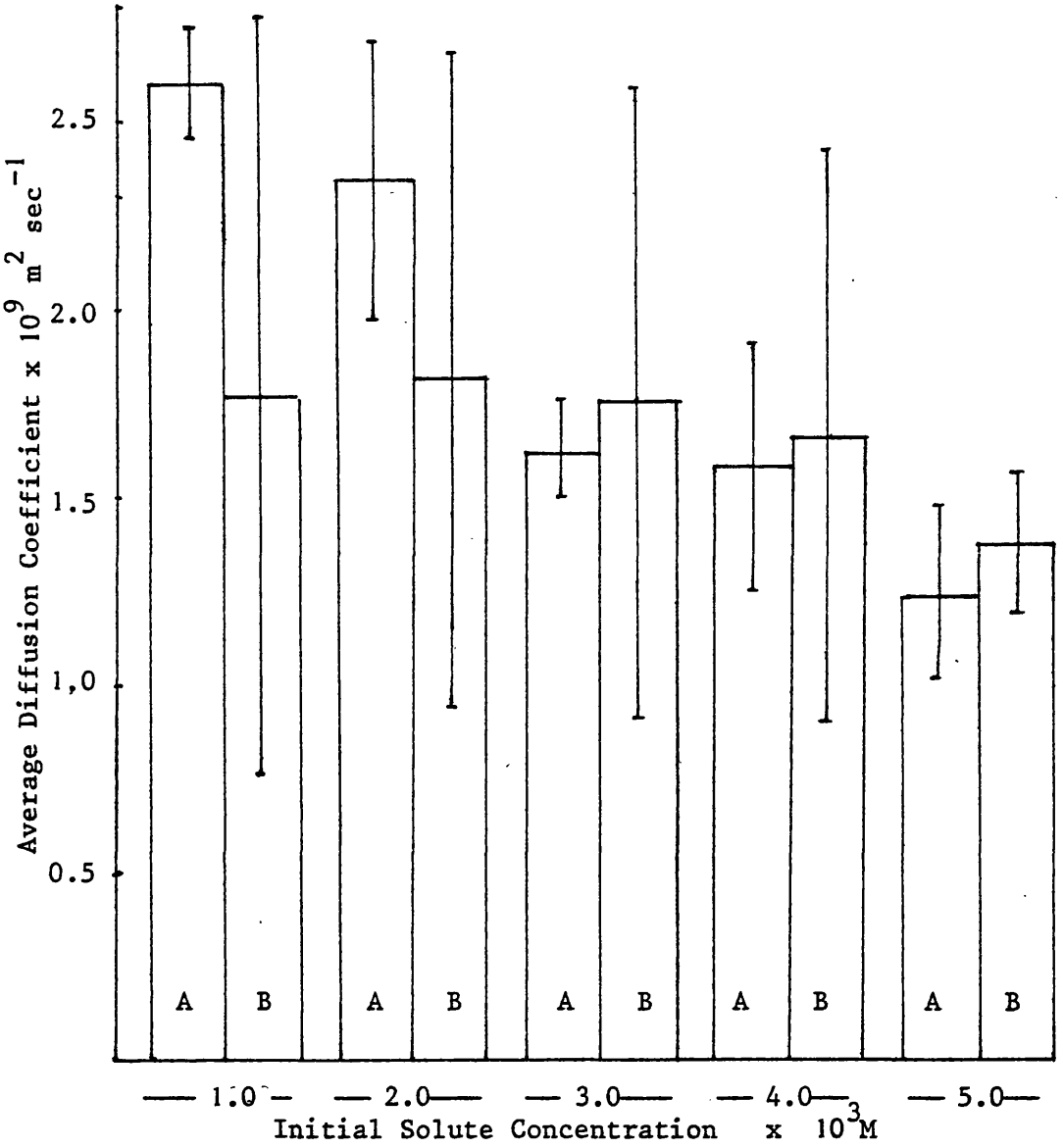


Fig 4.7: The Relationship Between the Average Diffusion Coefficient for the Sorption of 4-nitrophenol on to Active Carbon and the Experimental Conditions of Granule Weight and Initial Solution Concentration in the Liquid Phase.

A - 1.0 gramme B - 2.0 gramme

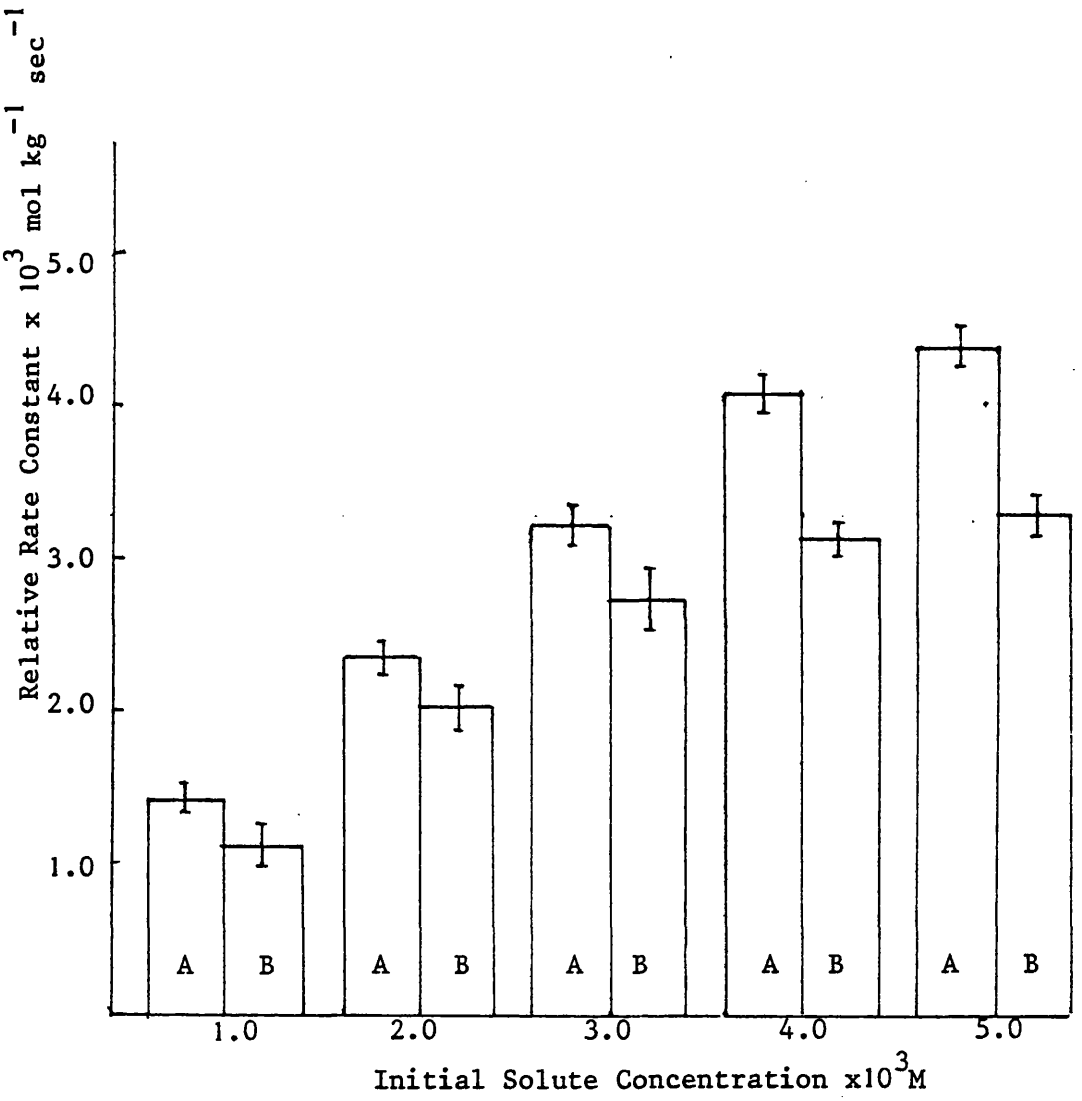


Fig 4.8: The Relationship Between the Relative Rate Constant for the Sorption of 4-nitrophenol on to Active Carbon and the Experimental Conditions of Granule Weight and Solute Initial Concentration in the Liquid Phase.

A - 1.0 gramme B - 2.0 gramme.

sorption isotherm data thus eliminating the adsorption component, an unbiased estimate of the true diffusive nature of the granular sorbent can be made.

It would appear from these studies that while the relative rate constant is a useful indicator of the absolute rate of solute uptake it tends to reflect the nature of the adsorption rather than diffusion process. The subspace model and the conservation of diffusing mass equation more correctly describe the mass transport of solute in the sorbent. An understanding of the nature of this process is of fundamental importance in the prediction of kinetic sorption behaviour. The results have shown that the average diffusion coefficient appears to be an invariant function of the adsorptive properties of the sorbent and, together with the isotherm constants, fully characterises the nature of the dynamic interaction.

The effect of solute structure was also studied using relative rate constant and average diffusion coefficient analysis. The data in table 3.38 shows that the rank order of relative rate constant is as follows :

4-nitrophenol > 4-methoxybenzoic acid > ethyl 4-aminobenzoate

Average diffusion coefficient data for the sorption kinetics of these three solutes is shown below in table 4.9. The values obtained suggest that no gross difference exists between the diffusion characteristics of the three model solutes as the average diffusion coefficients are all of a similar order of magnitude. It is possible that the rate of diffusion of 4-nitrophenol may be higher than the other two solutes as indicated by the higher average diffusion coefficient. If the concept of permeability is correct

Table 4.9 Average Diffusion Coefficient Data for the Sorption of Ethyl 4-aminobenzoate and 4-methoxybenzoic acid from 1000ml of Solution at 30^{o} and pH 2.32 (0.5 ionic strength) on to 1.0 gramme of Active Carbon.

Solute	Initial Concentration $\times 10^{3}$ M	Average Diffusion Coefficient $\times 10^{9} m^{2} sec^{-1}$	Standard Deviation $\times 10^{9}$	Coefficient of Variation %
4-nitrophenol	1.004 4.969	2.60 1.32	0.14 0.21	5.4 15.9
ethyl 4-aminobenzoate	0.985 4.925	0.94 0.34	0.53 0.12	56.4 35.3
4-methoxybenzoic acid	1.003	0.89	0.38	42.7

a higher average diffusion coefficient value would account for its higher relative rate constant with respect to 4-methoxybenzoic acid although its affinity for the carbon is lower.

4.2 BINARY SOLUTE SORPTION BEHAVIOUR.

4.2.1 Equilibrium Competitive Sorption Behaviour on Nylon 6 Powder.

Competitive sorption processes will probably not only reduce the capacity of a medicinal sorbent, but also reduce its rate of uptake as it would appear that the extent of sorption is an important determinant of the sorption kinetics (Section 4.1.2.3.2). Previous studies of competitive sorption processes have been concerned with active carbon adsorbents (Section 1.7) where the "competitiveness" of each component appears to be a function of their relative affinities and the concentration in which each species is present. Competitive sorption behaviour has not been previously reported for the sorption of weak or non-electrolytes in nylon polymers where the interaction arises due to matrix polymer chain penetration as opposed to adsorption on to a Langmurian type surface.

The K values for the sorption of ethyl 4-aminobenzoate and 4-methoxybenzoic acid from binary solute mixtures were found to be not significantly different from those of their corresponding single solute systems (table 3.14, figures 3.11 and 3.12). The isotherms of each solute were studied over the full range of their respective solubilities in binary solute solution and no competitive sorption effects were observed. This indicates that competition for sites in the nylon 6 matrix does not occur between these solutes which is consistent with the proposed association

interaction discussed previously in Section 4.1.2.1.1. Previous studies have shown that bound water is not essential for the sorption of ethyl 4-aminobenzoate by nylon 6 as C_1 type isotherms arise from sorption from dried n-hexane (Richardson 1973). If trace amounts of water are present in the solvent, S_1 type isotherms arise which are presumed to occur due to preferential sorption of water with displacement of ethyl 4-aminobenzoate. In aqueous solution the nylon 6 matrix will be highly hydrated, therefore, the benzoic acid derivatives probably bind by association with bound water together with a degree of stabilization arising between the hydrophobic moeities of the solute and polymer matrix. The number of bound water "sites" appears to remain limitless within the range of solubility of both of the benzoic acid derivatives, therefore, competitive sorption would not be expected to occur. If as suggested in Section 4.1.1.1 no displacement of water or inter-chain hydrogen bond cleavage occurs it is also unlikely that matrix disentanglement arises as has been suggested by Giles and his co-workers (1974). It is more probable that the benzoic acid derivatives diffuse into the matrix as it is disentangled by water molecules rather than by any specific effect of their own.
In contrast to the sorption of the benzoic acid derivatives, some degree of competitive sorption behaviour was observed in the binary solute systems involving phenol and 4-nitrophenol (figures 3.14 - 3.16). The sorption isotherm for 4-nitrophenol from single solute solution gave the characteristic C_2 type isotherm. On the addition of phenol to the solution, however, the isotherm for 4-nitrophenol was reduced and assumed the appearance of an L isotherm. The extent of the suppression in uptake is related to the concentration

of phenol present (figure 3.15). This suggests that the phenol is competing for interaction sites in the polymer that would otherwise be occupied by 4-nitrophenol molecules. Such competitive sorption interactions in polymers have apparently not been reported previously in the literature except with respect to the levelling process used in the commercial dyeing of polymers (Section 1.7.1 ·). The levelling process is only applicable when ionic dyes are used to colour synthetic polymeric materials and is not effective when unionised dyes are used which do not interact by an ion-exchange mechanism. In this study the phenolic compounds are both fully unionised.

The sorption of phenol is not affected by the presence of 4-nitrophenol at phenol : 4-nitrophenol initial concentration ratios of 1:1 and 3:1. This may again be explained by phenol being able to bind more strongly with the nylon 6 with the result that it is preferentially sorbed and consequently does not suffer competition. Similarly, the sorption of ethyl 4-aminobenzoate and 4-methoxybenzoic acid in the presence of phenol did not indicate the presence of any competitive sorption effects (Table 3.25). Increasing the concentration ratio of phenol to 4-nitrophenol to 5:1 did, however, result in a change in isotherm type for both solutes. (Figure 3.16). The isotherm for phenol in this system is initially linear and closely follows that of the isotherm determined from single solute solution. At an uptake of approximately 2.5 mol Kg^{-1} there is a large increase in sorption of phenol relative to its single solute uptake. The isotherm for 4-nitrophenol shows an initial reduction in uptake due to the influence of phenol but again at an uptake value of about 1.5 mol Kg^{-1} the extent of sorption shows a

large increase. This anomalous isotherm type has been termed the Z type isotherm by Giles (Giles and Tolia 1964) and has been reported for the sorption of 4-nitrophenol by dry cellulose from 2.2.4-trimethylpentane. This was explained in terms of a sudden partial breakdown of the cellulose structure due to solute penetration, when the solute concentration is raised above a given value. In the case of the sorption of the phenols by nylon 6 powder this critical value occurs above about 4 mol Kg^{-1} total phenols uptake. The large relative increase in uptake beyond this point was accompanied by a change in the morphology of the polymer powder. At the point at which Z isotherm behaviour arose the powder particles congealed into a cohesive rubbery mass. It may be, therefore, that at high concentration of the mixed phenols the nylon 6 is becoming plasticized. Each solute in this case is acting as a co-plasticizer as neither can effect the structural changes at the level of concentration in which they are present individually.

The appearance of competitive sorption behaviour in this systen together with plasticization emphasizes the difference in the interaction mechanism between the benzoic acid and phenolic derivatives. Phenol and 4-nitrophenol probably form hydrogen bonds of sufficient intensity to displace bound water from amide groups in the matrix and associate with them directly. This would account for the high K values obtained even though their aqueous solubilities are also high compared to those of the benzoic acid derivatives. Previous studies have shown that phenol can completely dissolve the nylon 6 matrix (Marcus 1959) whereas this study has demonstrated that the C_2 type isotherm for 4-nitrophenol indicates that it is unlikely to give rise to plasticization, and subsequent dissolution of the

polymer. Studies by Bark and Graham (1967) on the interaction of phenolic solutes with nylon T.L.C stationary phases have shown that they bind to polyamides by hydrogen bond formation between the hydroxyl group and the amide group of the polymer chain. The electron density in the region of the OH group on the 4-nitrophenol molecule will be less than that on phenol due to the electron withdrawing action of the nitro group. This might account for the displacement of 4-nitrophenol by phenol and the inability of the former solute to form hydrogen bonds of sufficient strength to disentangle the crystalline regions of the nylon matrix and eventually dissolve it. The co-plasticization behaviour probably arises due to the partial plasticization of the crystalline regions of the matrix by phenol. The results suggest that 4-nitrophenol can enhance the plasticizing activity of phenol in a weakened matrix although it is, by itself, unable to elicit such structural changes.
The essential difference between the competitive interactions of the phenolic and benzoic acid derivatives appears to centre around the nature of the binding site. As the benzoic acid derivatives probably associate with bound water, the "sites" are effectively unlimited and the uptake of each solute remains a function of its activity in the bulk solution phase. The phenolic derivatives, however, bind to a finite number of amide linkages in the matrix. As these become limited, the two solutes compete for the remaining available sites and a suppression of the uptake of the more weakly interacting solute occurs. In the case of sorption on to nylon 6 an additional consequence of site limitation is plasticization. As phenols probably interact by a mechanism of interchain hydrogen bond cleavage, the sorption of a critical number of phenol molecules

on to a limited number of sites results in plasticization in addition to competitive sorption behaviour.

4.2.2. Equilibrium Competitive Sorption Behaviour on Active Carbon.

Unlike competitive sorption processes in polymeric sorbents, the interaction of solutes from binary mixed solution with active carbon has been the subject of previous studies (Section 1.7.2).

A different format for making the binary mixed solutions was adopted as compared to that used in the nylon 6 sorption study; the initial concentration of one solute was varied in the presence of a constant concentration of the second. To facilitate comparison with studies in the literature the formulation of the mixed solute solution was changed from the constant initial concentration ratio solutions used in the nylon 6 studies to that described above. Reports in the literature on the sorption of binary solute mixtures by sorbents have previously been concerned with the prediction of binary solute sorption using single solute sorption data (Section 1.7.2). These reports suggest that the "competitiveness" of a solute in binary system is a function of the relative affinity and concentration with respect to the competing species. It would follow, therefore, that for two solutes of identical affinity the preferentially adsorbed solute would be that present in higher concentration. Furthermore, if two solutes were present in identical concentration the solute with higher affinity for the surface would be preferentially adsorbed (Weber and Morris 1964). The sorption isotherms for mixtures of 4-nitrophenol and phenol were found to follow these general predictive rules. From the single solute isotherm data (figure 3.22) the affinity of 4-nitrophenol is greater than that for phenol and in the presence of

4-nitrophenol the sorption of phenol is reduced (figure 3.25). The extent of the reduction of the sorption of phenol increases as the concentration of 4-nitrophenol present rises. The extent of suppression can be visualised by defining a suppression factor :

$$S = \frac{n_{\text{binary solute}}}{n_{\text{single solute}}} \quad \ldots\ldots\ldots\ldots (4.17)$$

where S = suppression factor at specified equilibrium concentration

$n_{\text{binary solute}}$ = the uptake of solute from binary mixed solution

$n_{\text{single solute}}$ = the uptake of solute from single solute solution

Table 4.10 Suppression Factor Data for the Sorption of Phenol in the Presence of 4-nitrophenol at 4×10^{-3} M Equilibrium Concentration.

Initial Concentration of 4-nitrophenol	Phenol Suppression Factors
10^{-3} M	0.40
3×10^{-3} M	0.61
5×10^{-3} M	0.74

Table 4.10 shows that although competitive sorption increases as the competitor concentration rises the effect of increasing concentration of 4-nitrophenol on the uptake of phenol is relatively less marked. Figure 3.28 shows that 4-nitrophenol will suppress the uptake of phenol (initial concentration 5×10^{-3} M) even over the low concentration range of zero to 10^{-3} M. Table 4.10 shows that increasing the initial concentration of competitor, in turn increases the

suppression of phenol. The relationship between the initial concentration of 4-nitrophenol and the phenol suppression factor suggests that competitive sorption may be becoming limited. This suppression factor data shows that increasing the competitor concentration from 0 to 10^{-3} M reduces the uptake of phenol by 40%. A further increase of initial concentration by $2x10^{-3}$ M to $3x10^{-3}$ M results in an additional 21% reduction in activity. Increasing by the same initial concentration increment to $5x10^{-3}$ M only increases the degree of suppression by a further 13%. Again the extent to which the uptake of phenol is reduced increases as the concentration of 4-nitrophenol is increased. The presence of phenol in this system has no effect on the sorption of 4-nitrophenol (figures 3.26 and 3.27). Similar findings on the sorption of mixtures of phenols have been reported by Fritz and Schluender (1974)and Jossens et al (1978). The apparent lack of competitiveness of phenol suggests that the true affinity of 4-nitrophenol for the sorption sites on active carbon is far higher than would be predicted from the sorption isotherm. One possible explanation may be based on a difference in solute-sorbent binding intensity for phenol and 4-nitrophenol. Mattson and Mark (1971) have suggested that aromatic compounds predominantly adsorb on to active carbon by an electron donor-acceptor complex mechanism between surface oxides and the electron system of the solute. These donor-acceptor complexes would be expected to be reversible and, due to the involvement of the electrons of the aromatic nucleus, the solute would be expected to adsorb in a "face-on" orientation. The electron density in the π electron cloud of 4-nitrophenol is much greater than that of phenol due to the electron withdrawing nature of the para nitro group. As

a result of the difference in π cloud electron density it may be, therefore, that 4-nitrophenol interacts more strongly with the carbon surface than phenol with the result that 4-nitrophenol will not experience strong competition from phenol molecules.

The sorption of 4-methoxybenzoic acid in the presence of 4-nitrophenol or ethyl 4-aminobenzoate again follows the general principles of "competitiveness" outlined above. The affinity of 4-nitrophenol and ethyl 4-aminobenzoate for the carbon is similar (as determined from their single solute isotherms) and their suppression of the uptake of 4-methoxybenzoic acid would, therefore, be expected also to be similar. Comparison of figures 3.29 and 3.33 show that the suppression experienced by 4-methoxybenzoic acid in the presence of ethyl 4-aminobenzoate is considerably greater than in the presence of 4-nitrophenol at the higher concentrations of competing species. Table 4.11 summarises the effect of ethyl 4-aminobenzoate and 4-nitrophenol concentration on the sorption of 4-methoxybenzoic acid. The increase in the degree of competition experienced by 4-methoxybenzoic acid in the presence of ethyl 4-aminobenzoate is also reflected in a change in isotherm type (figure 3.34).

In all of the other systems studied the isotherms remained of the L-type in the presence of the competing species. The isotherm for 4-methoxybenzoic acid in the presence of 10^{-3} M ethyl 4-aminobenzoate is L_1 in nature and on increasing the competitor concentration to 3×10^{-3} M then 5×10^{-3} M, the isotherms change through C_1 type to S_1 type. Giles (1960) has suggested that S isotherms may be produced by competition from solvent molecules or a second solute in the solvent present as a trace contaminant (Section 1.5.2.3).

It is probable that the isotherm change observed for 4-methoxybenzoic

Table 4.11 Suppression Factor (Equation 4.17) Data for the Sorption of 4-methoxybenzoic acid in the Presence of Ethyl 4-aminobenzoate and 4-nitrophenol at 4×10^{-3} M Equilibrium Concentration.

Initial Concentration ethyl 4-aminobenzoate	4-methoxybenzoic acid Suppression Factor	Initial Concentration 4-nitrophenol	4-methoxybenzoic acid Suppression Factor
10^{-3} M	0.40	10^{-3} M	0.40
3×10^{-3} M	0.81	3×10^{-3} M	0.53
5×10^{-3} M	0.91	5×10^{-3} M	0.72

acid is due to strong competition from ethyl 4-aminobenzoate, which again is far higher than would be expected from the single solute isotherm. The high competitiveness of ethyl 4-aminobenzoate may be explained by its state of ionisation; at pH 2.32 ethyl 4-aminobenzoate is approximately 36% unionised. It would appear that the isotherm misrepresents the true extent of the sorption of ethyl 4-aminobenzoate as the affinity for an effective concentration in the adsorbed phase is higher than would be predicted from the isotherm with respect to that of 4-nitrophenol It is possible that the ethyl 4-aminobenzoate molecule can occupy a larger effective area by neutralising surface oxide groups which would otherwise be available to participate in change transfer complexes with 4-methoxybenzoic acid This would result in a higher degree of displacement of competing species also present in the sorption system

The single point plot data for the above systems (figures 3.31 and 3.35) indicates that the uptake of both solutes in the binary solute 4-methoxybenzoic acid : 4 nitrophenol and 4-methoxybenzoic acid : ethyl 4-aminobenzoate systems is reduced. This is in contrast to the phenol : 4 nitrophenol binary solute system where the sorption of 4-nitrophenol was unaffected by the presence of phenol The single point plots also indicate that where competitive sorption occurs, the extent of the reduction in uptake is a function of the concentration of competitor present in the system.

If competitive sorption is dependent on such factors as solute affinity and concentration it might be expected that some form of predictive method for determining competitiveness might be developed. Several procedures have been previously used with varying degrees of

success as outlined in Section 1.7.2. Many of these methods rely on the adsorption system behaving according to Langmuir's model of adsorption. If predictive methods based on the Langmuir equation are to be successully employed, the values of n_{max} obtained from single solute sorption studies must be reliable. The n_{max} values for the two solutes which are the subject of the prediction must also not be significantly different. Although the isotherm data obtained in this study can be fitted to the Langmuir equation satisfactorily, the reliability of the n_{max} values is doubtful as uptake was not studied in the region of maximum uptake in all cases. The n_{max} value for 4-nitrophenol can be considered to be a satisfactory estimate of the maximum uptake as the isotherm determination was extended over the range of uptake where a plateau arises. This was not the case for 4-methoxybenzoic acid, ethyl 4-aminobenzoate and phenol where the isotherm was determined over the L_1 isotherm region only A newer nethod of prediction has been developed which utilises single solute data but is not restricted to a specific theoretical model such as the Langmuir surface (Radke and Prausnitz 1972b), Their calculation procedure uses a classical thermodynamic approach and was developed from ideal solution theory, The adsorbed phase is considered to behave as an ideal solution where the interfacial tension of the binary solute adsorbed phase is a weighted average of the interfacial tensions of the two single solute adsorbed phases. Single solute isotherm data is used to calculate the interfacial tension of the adsorbing species using Gibbs' isotherm equation. Full details of the calculation procedure are given in Section (1.7.2) and the computer program used to generate the binary

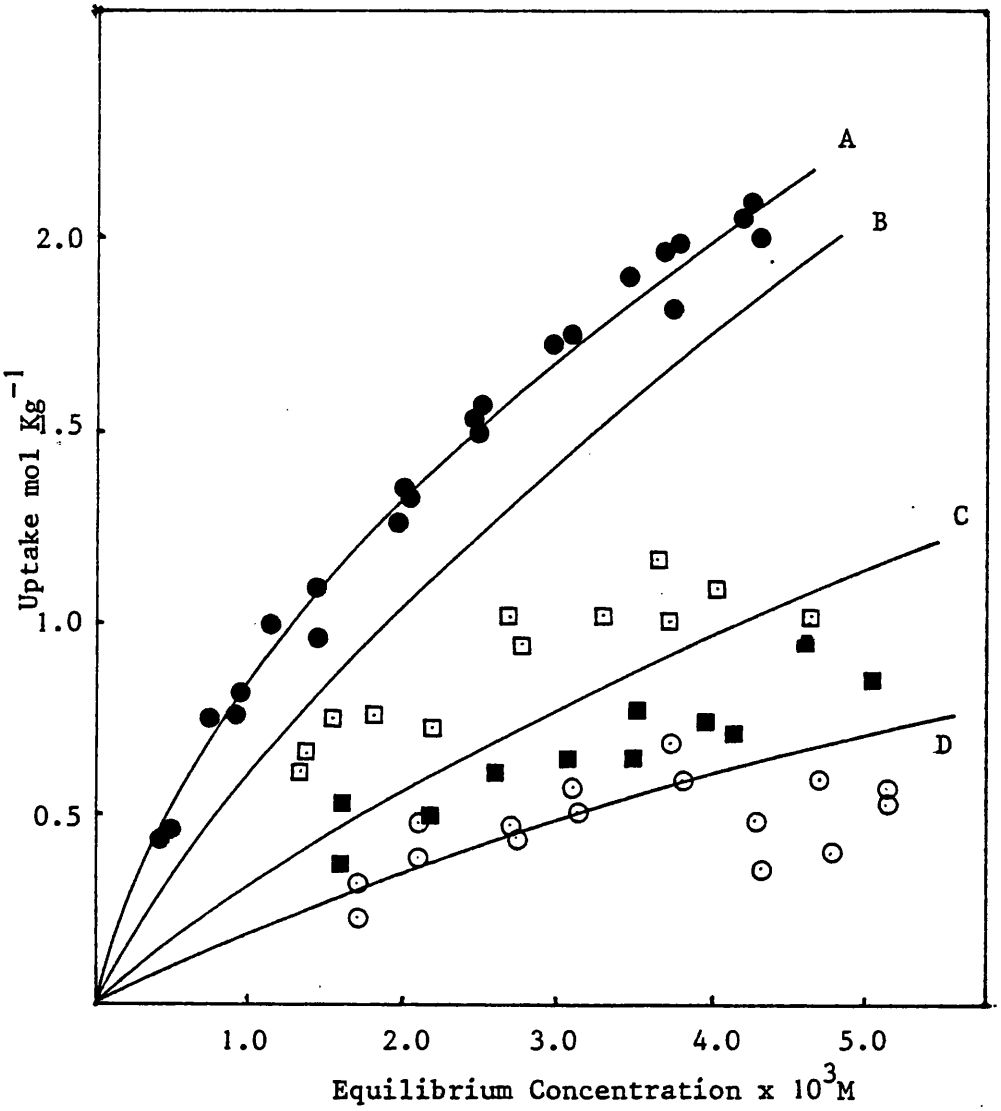


Fig 4.9 Experimental and Theoretical Isotherms for the Sorption of 0 - 10^{-3}M Phenol by Active Carbon in the Presence of 4-nitrophenol at pH 2.32 (0.5M ionic strength) and 30°.

Key:	4-nitrophenol Concentration	Predicted Isotherm	Experimental Sorption Data
	Zero	A	●
	10^{-3}	B	□
	3×10^{-3}	C	■
	5×10^{-3}	D	○

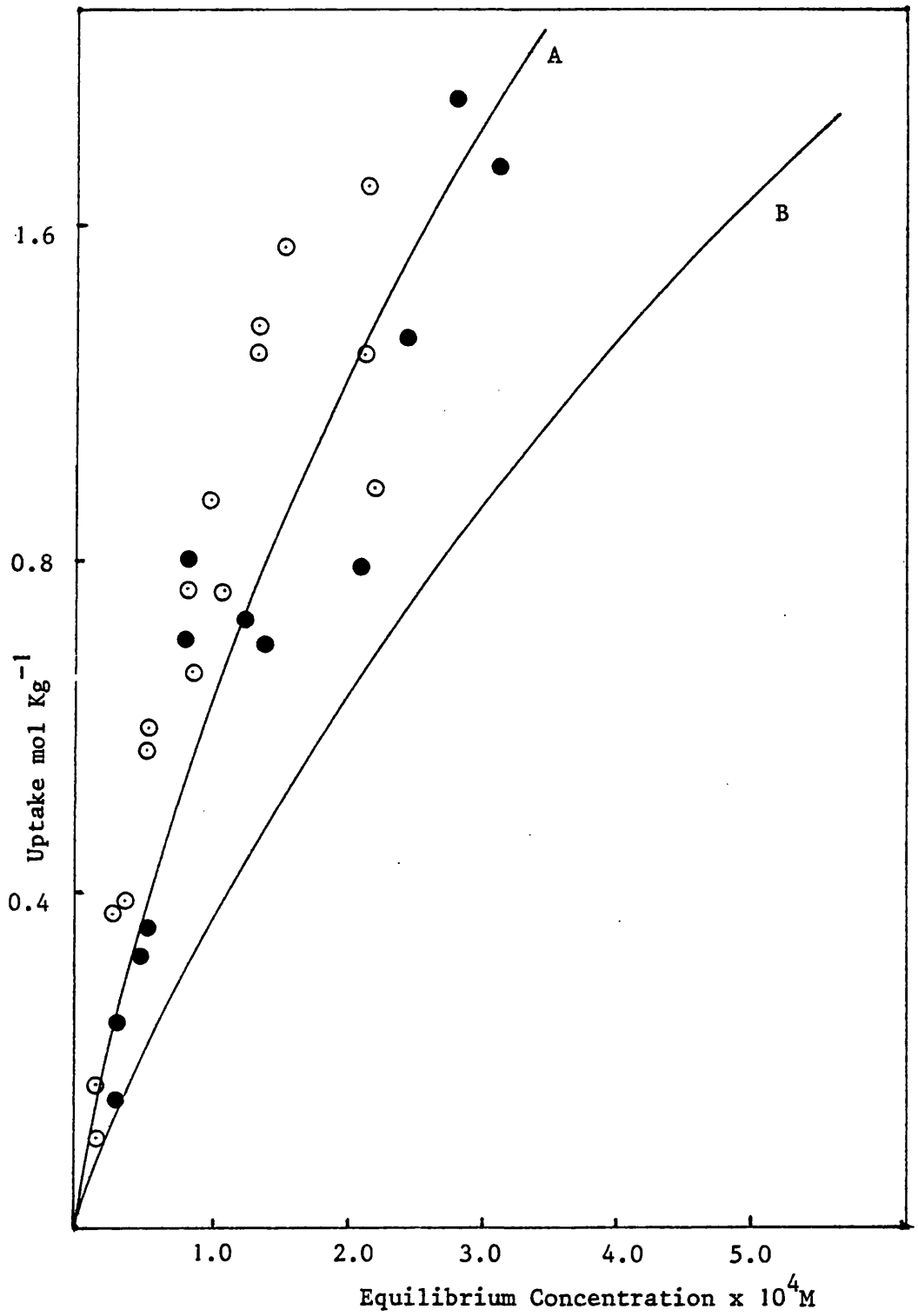


Fig 4.10: Experimental and Theoretical Isotherms for the Sorption of 0 - 10^{-3}M 4-nitrophenol in the Presence of 5×10^{-3}M Phenol at pH 2.32 (0.5M ionic strength) and 30°.

Key:	Phenol Concentration	Predicted Isotherm	Experimental Data
	Zero	A	●
	5×10^{-3}	B	○

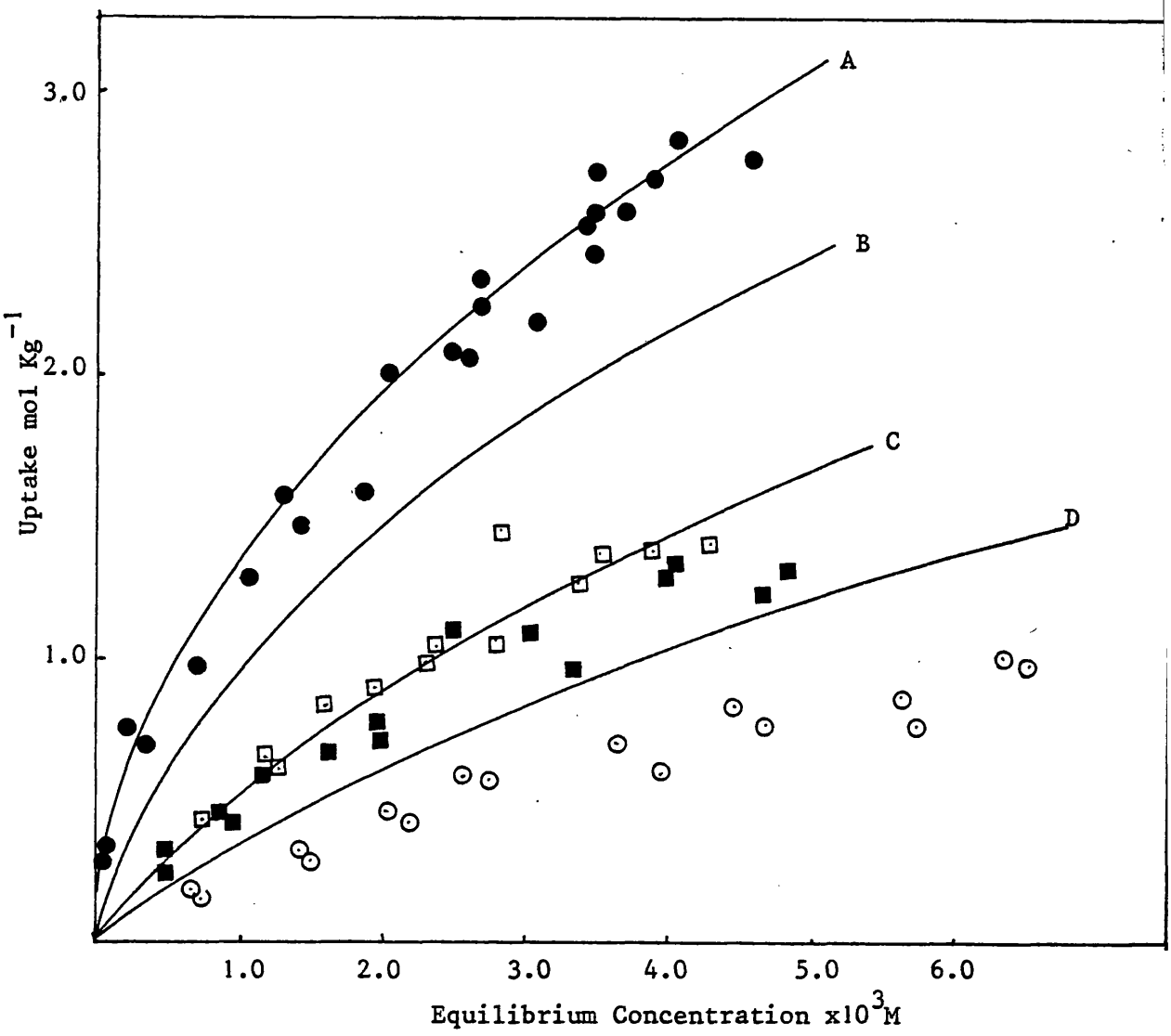


Fig 4.11: Experimental and Theoretical Isotherms for the Sorption of 0 - 10^{-3}M 4-methoxybenzoic acid by Active Carbon in the Presence of 4-nitrophenol at pH 2.32 (0.5M Ionic Strength) and 30°.

Key: 4-nitrophenol Concentration	Predicted Isotherm	Experimental Sorption Data
Zero	A	●
10^{-3}	B	□
3×10^{-3}	C	■
5×10^{-3}	D	○

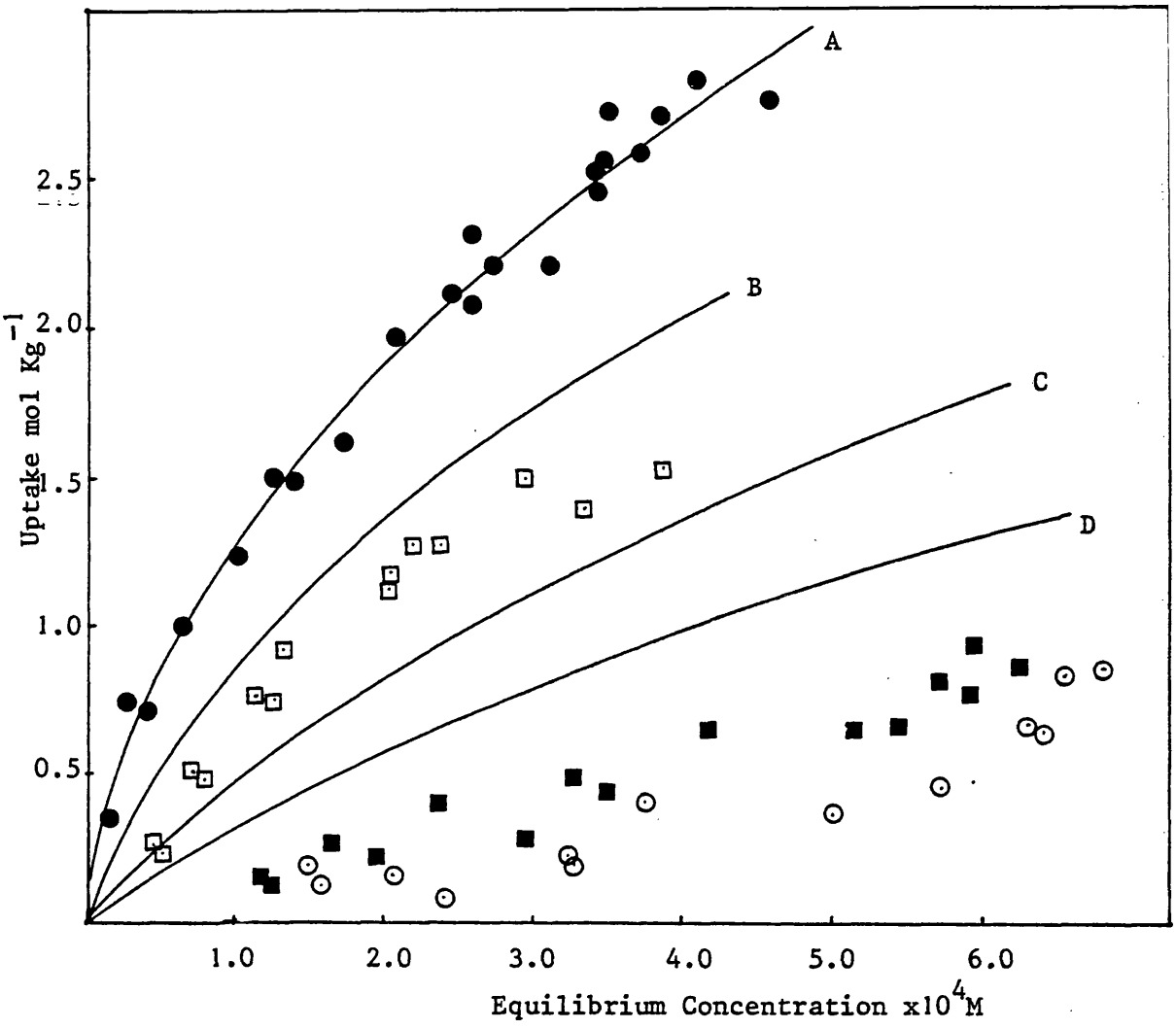


Fig 4.12 : Experimental and Theoretical Isotherms for the Sorption of 0 - 10^{-3}M 4-methoxybenzoic acid by Active Carbon in the Presence of ethyl 4-aminobenzoate at pH 2.32(0.5M Ionic Strength) and 30°.

Key: ethyl 4-aminobenzoate Concentration	Predicted Isotherm	Experimental Sorption Data
Zero	A	●
10^{-3}	B	□
3×10^{-3}	C	■
5×10^{-3}	D	○

solute solution sorption isotherms is given in Appendix 4. An exhaustive and comprehensive comparison of Langmurian and ideal solution theory based predictive methods has suggested that the latter procedure is probably the most satisfactory and widely applicable (Everett 1979). Attempts were therefore made to use this procedure to assess the accuracy with which likely competitive sorption phenomena may be predicted; theoretical sorption isotherms with the experimental data are shown for several binary solute systems in figures 4.9 to 4.12. Suppression factors (Equation 4.17) for the theoretical and experimentally determined binary solute isotherms are given in table 4.12.

Typically. the theoretical isotherms show that increasing the concentration of competitor present suppresses the sorption of the other solute. The isotherms for phenol and 4-methoxybenzoic acid in the presence of 4-nitrophenol (figures 4.9 and 4.11 respectively) show poor agreement at low concentration of competitor, but at high concentration the theoretical curves are much closer to those determined experimentally The theoretical isotherms for the sorption of 4-methoxybenzoic acid in the presence of ethyl 4-aminobenzoate show a low degree of agreement with the experimental isotherms and do not predict the change in isotherm type found in this system. The procedure indicates that the sorption of 4-nitrophenol should be suppressed to some extent by the presence of phenol, experimentally however, this was not observed.

It is apparent, therefore, that this calculation procedure may be of some use in predicting generalised competitive effects but is not satisfactorily accurate to obviate the need for direct experimentation. The inaccuracies of the calculation method are probably associated

Table 4.12 Suppression Factors for the Sorption of the Model Solutes on to Active Carbon from Binary Solute Solution As Determined from Isotherm Data Obtained by Experimentation and Prediction Using Ideal Solution Theory.

Solute	Competitor	Competitor Concentration	Equilibrium * Concentration	Solute Suppression Factor	
				Experimental	Theoretical
Phenol	4-nitrophenol	10^{-3} M	4×10^{-3} M	0.55	0.88
		3×10^{-3} M	4×10^{-3} M	0.35	0.47
		5×10^{-3} M	4×10^{-3} M	0.30	0.30
4-nitrophenol	Phenol	5×10^{-3} M	5×10^{-4} M	1.00	0.57
4-methoxybenzoic acid	4-nitrophenol	10^{-3} M	4×10^{-3} M	0.52	0.85
		3×10^{-3} M	4×10^{-3} M	0.41	0.53
		5×10^{-3} M	4×10^{-3} M	0.24	0.39
4-methoxybenzoic acid	ethyl 4-amino-benzoate	10^{-3} M	4×10^{-3} M	0.59	0.75
		3×10^{-3} M	4×10^{-3} M	0.22	0.69
		5×10^{-3} M	4×10^{-3} M	0.11	0.37

* The equilibrium concentration of solute at which the suppression factor was calculated.

with non-ideality with respect to ideal solution theory or errors implicit in the calculation procedure. It is likely in these sorption systems where high surface activity arises that the activity rather than the concentration in the adsorbed phase should be used in the calculation procedure. Non-ideality with respect to ideal solution theory is also likely to occur if the solutes are capable of interacting with one another at the surface. If this were to occur it would be unlikely that an accurate prediction of binary solute sorption equilibria could be achieved on the basis of single solute isotherm data. The calculation procedure was implemented using a computer program supplied by the originators of the theory (Jossens; personal communication; Appendix 4). The computer program uses the constants of a given isotherm equation to represent the single solute isotherm. The Langmuir equation was used in the calculation procedure as the Radke equation could not be conveniently utilised without extensive modification to Jossen's original algorithm.

4.2.3 Dynamic Competitive Sorption Behaviour on Active Carbon.

Several reports in the literature have shown that the rate of uptake of organic solutes from aqueous solution is affected by the presence of a competing species (Section 1.8.1). Figures 3.59, 3.61, 3.63 and 3.65 show that the overall rate of sorption for a given solute is suppressed, with respect to the single solute sorption, in the presence of a solute where competitive sorption has been shown to occur. Difficulties arise, however, if attempts are made to numerically compare rates of uptake for the model solutes from binary and single solute solution. Figure 3.58 shows that the slope of the $t^{\frac{1}{2}}$ plot for 4-nitrophenol is reduced in the presence of ethyl 4-aminobenzoate, but intercepts on the ordinate as opposed

to the abscissa (Figure 3.58). The nature of the $t^{\frac{1}{2}}$ plot appears to differ for single and binary solute solutions in this respect suggesting that it may not be a reliable method of comparing rate data. As the equilibrium uptake of the solute changes in the binary solute systems, calculation of average diffusion coefficients is not possible using techniques presently available.

The method of Crank outlined in Appendix 3, relies on the ability to use experimentally determined isotherm constants to assess the effect of the sorption process on permeability. As the equilibrium isotherm generally changes in the presence of competing species, the sorption component is difficult to take into consideration. An alternative method of analysing the data is by means of the suppression factor (Equation 4.17) which represents the fractional reduction in uptake with respect to the single solute kinetic profile. This value is numerically similar to those calculated for the equilibrium binary solute sorption studies, however, the dynamic suppression factor, S_t, describes the non-equilibrium situation. Instead of the numerical value being defined at specified equilibrium concentrations, therefore, the suppression factors are specified with respect to time. Five values of S_t were calculated over the 300 minute experimental time interval after 50, 100, 150, 200 and 250 minutes. These values were found to be approximately equal, therefore a mean suppression value was calculated to reduce the effect of competition to a single parameter (table 4.13). The two major factors influencing the equilibrium competitiveness of a solute are the relative affinity and concentration with respect to its competitor. It is apparent from table 4.13 that the relative initial concentration of the solute and its competitor is a major determinant of the extent of suppression.

Table 4.13 Suppression Factors for the Sorption of the Model Solutes in the Presence of Competing Species with Respect to Time.

Solute	Competitor	Initial Concentration* Ratio	S_t (Mins) Elapsed Time 50	100	150	200	250	Mean
ethyl 4-aminobenzoate	4-nitrophenol	0.2	0.52	0.45	0.43	0.38	0.37	0.43
4-methoxybenzoic acid	4-nitrophenol	0.2	0.29	0.35	0.34	0.32	0.29	0.32
4-nitrophenol	ethyl 4-aminobenzoate	0.2	0.52	0.55	0.54	0.54	0.54	0.54
4-methoxybenzoic acid	ethyl 4-aminobenzoate	0.2	0.48	0.48	0.46	0.45	0.45	0.46
4-nitrophenol	ethyl 4-aminobenzoate	5.0	0.16	0.17	0.22	0.14	0.13	0.16
4-nitrophenol	4-methoxybenzoic acid	5.0	0.19	0.20	0.19	0.18	0.17	0.19
ethyl 4-aminobenzoate	4-nitrophenol	5.0	0.00	0.00	0.00	0.00	0.00	0.00
ethyl 4-aminobenzoate	4-methoxybenzoic acid	5.0	0.09	0.04	0.05	0.03	0.05	0.05

* Initial Concentration Ratio = Initial Concentration-Solute/Initial Concentration-Competitor.

When the solute is present in a concentration five times that of the competing species little suppression of uptake occurs. When the solute is present at one-fifth the concentration of the competitor the kinetic profile is reduced by between half and one-third. In the dynamic system, the affinity remains constant, whereas the concentrations of the two species change with respect to time. Thus for example when 4-nitrophenol is present in the binary system at an initial concentration five times that of ethyl 4-aminobenzoate the effect of the relative concentration component of the competitiveness will be accentuated by the higher rate at which it is taken up by the carbon. This is also illustrated in the systems where 4-methoxybenzoic acid is present at an initial concentration ratio of 0.2 (Table 4.13) i.e. at a lower concentration with respect to its competitor. Ethyl 4-aminobenzoate has been shown to exert a higher suppression on the equilibrium uptake of 4-methoxybenzoic acid than 4-nitrophenol. The mean suppression ratio of 4-methoxybenzoic acid is, however, 0.32 in the presence of 4-nitrophenol and 0.46 in the presence of ethyl 4-aminobenzoate. This discrepancy can be accounted for by a consideration of the relative rates of sorption for ethyl 4-aminobenzoate and 4-nitrophenol. The latter solute has the higher rate of sorption, and, although it is less competitive in the equilibrium binary system it is more competitive in the dynamic situation.

The conservation of diffusing mass equation (equation 1.3.7) suggests that the overall rate of sorption of each solute in the binary system may be affected by competitive effects on the adsorption and diffusion component. The average diffusion coefficients for each solute are similar (table 3.9) indicating that the rate of

permeation through the carbon is determined mainly by the characteristics of the sorption isotherm. It is therefore possible that the competitive sorption process is the most likely influence on rate suppression. It is also likely that solute molecules may sterically hinder one another whilst diffusing through the solvent filled pores. It is not possible to assess whether this mechanism plays a significant role in the lowering of the overall solute sorption rate in the binary solute systems used in this study.

4.3 THE CHARACTERISTICS AND SORPTION BEHAVIOUR OF NYLON 6 COATED ACTIVE CARBON.

4.3.1 The Morphological and Physical Characteristics of Nylon 6 Coated Active Carbon.

The physical tests carried out on the nylon 6 coated active carbon granules indicated that the coat did not profoundly affect the nature of the core carbon (Section 2.7.3). Heats of wetting (Section 2.7.3.2) and saturation vapor uptakes (table 2.7) were not significantly different suggesting that the coating did not introduce selectivity based on simple size exclusion processes. Mercury porosimeter studies did indicate that some difference exists between the coated and uncoated carbon. The initial phase of the porogram for the coated sorbent shows that no mercury is penetrating the composite granule, however it superimposes upon the uncoated program at higher pressures (lower pore radius) as shown in figures 2.7 and 2.8. It is not clear whether this result was representative of a change in porosity or an artifact of disruption of the coat followed by impaction of the resulting debris into the pore network.

The presence of the nylon 6 coating is clearly seen in plate 4.5 at

times 66 magnification. The finely pitted surface, characteristic of the uncoated granule (plate 4.2), is replaced by a smooth surface perforated by small circular craters. Larger fissures are still apparent although the smaller ones appear to be bridged by the polymer coat. If plate 4.6, the coated active carbon magnified 662 times, is compared with plate 4.3, it is apparent that the characteristic small fissures are obscured by the polymer film and have been replaced by new surface features illustrated schematically in figure 4.10; of particular interest are the presence of what appears to be numerous small pinholes and blisters. The pinholes may be a result of blisters in the coat which have burst. As the samples were coated with gold, under vacuum, prior to being scanned, the blisters and pinholes may be present as a result of the preparation process, particularly if any air is trapped underneath the coat. The light, spherical particles are probably spray-dried nylon 6.

If the surface of the coated granules is examined at a high magnification of times 21,900 (plate 4.7) it can be seen that the surface is smooth and completely covers the granule surface. Attempts were made to fracture the coated granules, and a typical micrograph after such treatment is shown in plate 4.8 at a magnification of times 2,800. This shows that the nylon 6 coat is only covering the surface of the granule and does not penetrate the internal pore structure. The thickness of the coat, as estimated from the torn edges appears to be about 0.5μm.

4.3.2 Sorption Behaviour.

Studies of the influence of polymeric coatings on the sorption of solutes have been predominantly related to their use in haemoper-

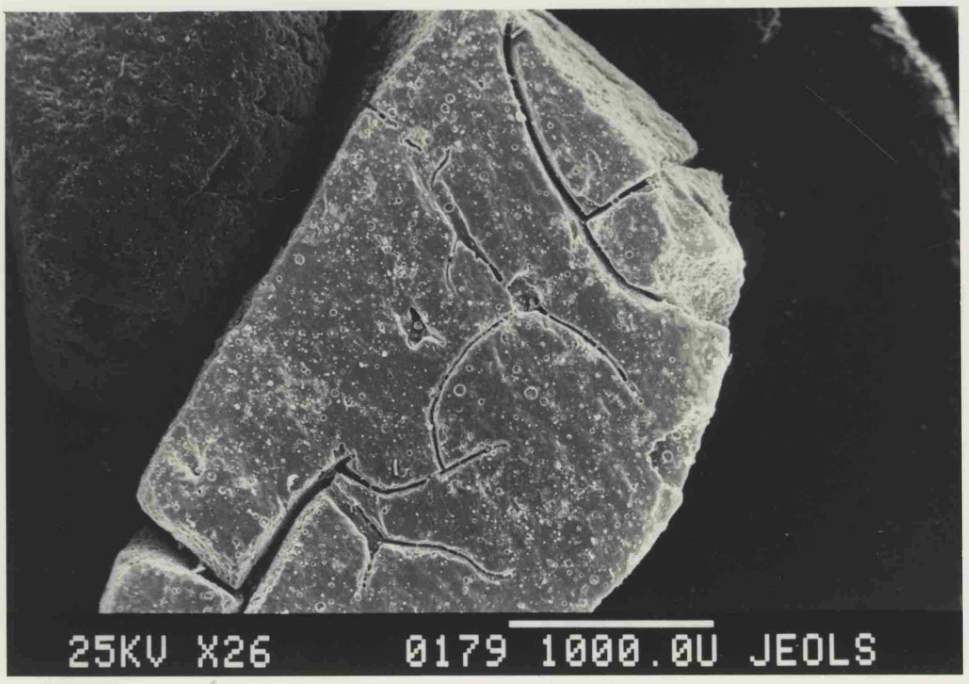
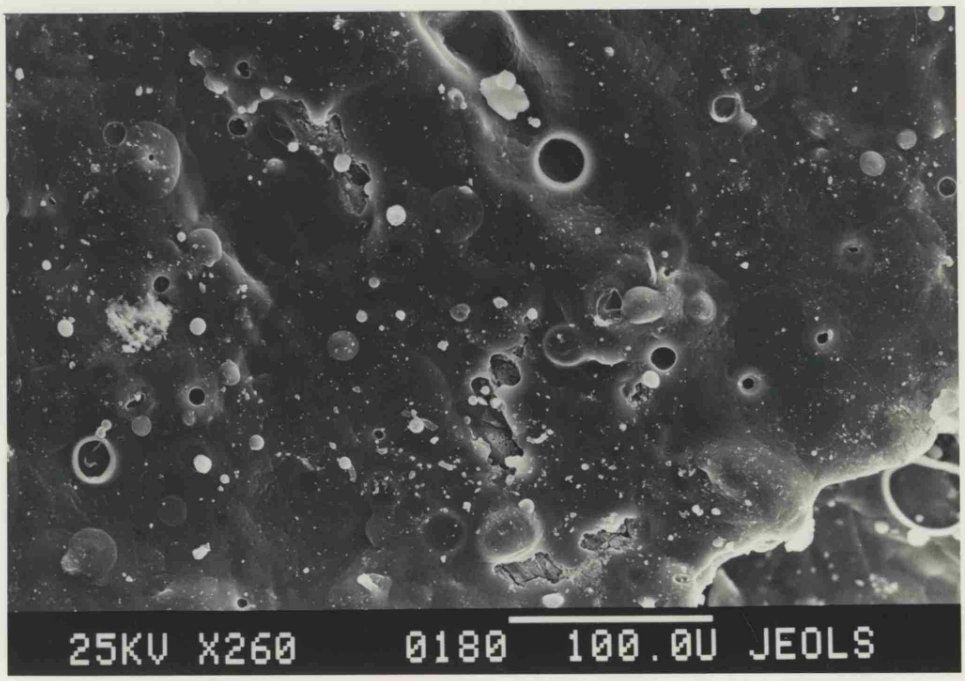


Plate 4.5 Nylon 6 Coated Active Carbon x 66 Magnification.

(1000μm)



(100μm)

Plate 4.6: Nylon 6 Coated Active Carbon, Magnified 662 times

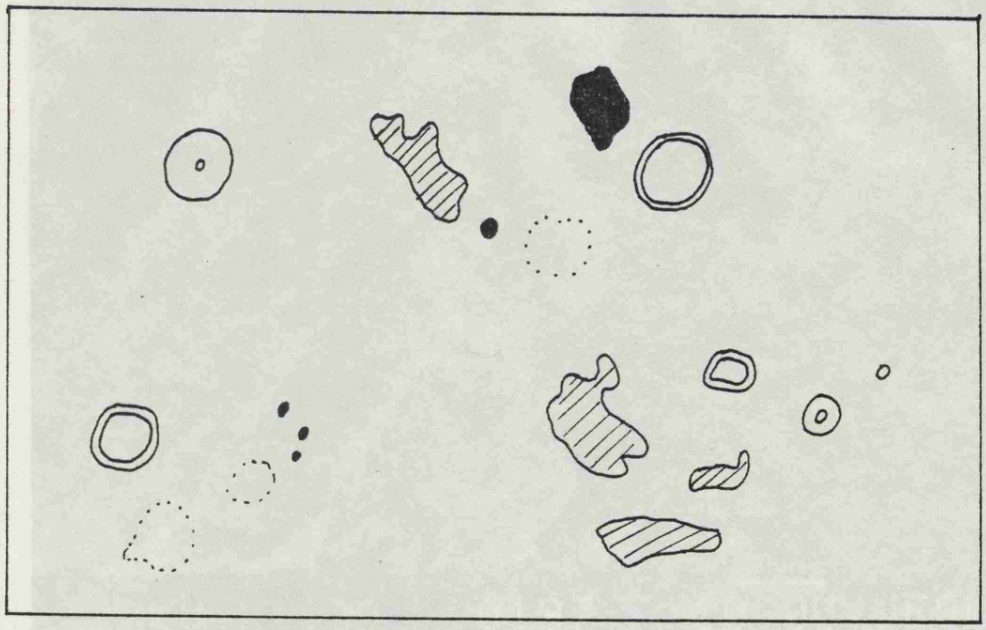


Figure 4.13: Surface Features of Plate 4.6

Pinholed blister in low stress region of the coat

Pinholed blister in the high stress region of the coat

Tear

Blister

Spray-Dried Nylon 6

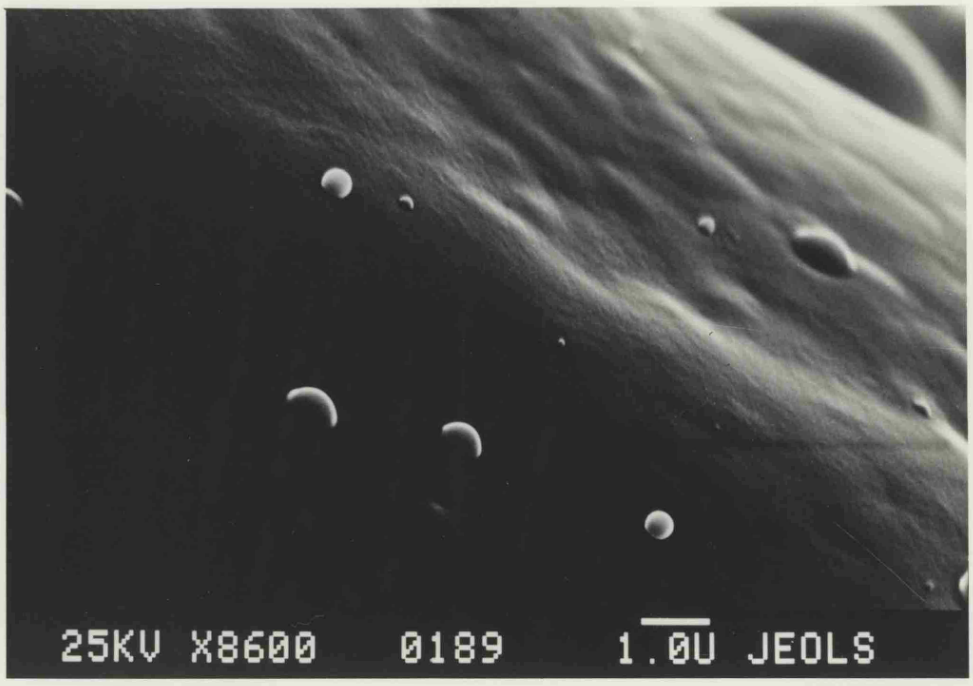


Plate 4.7 Nylon 6 Coated Active Carbon x 21,900 Magnification.

(1 μm)

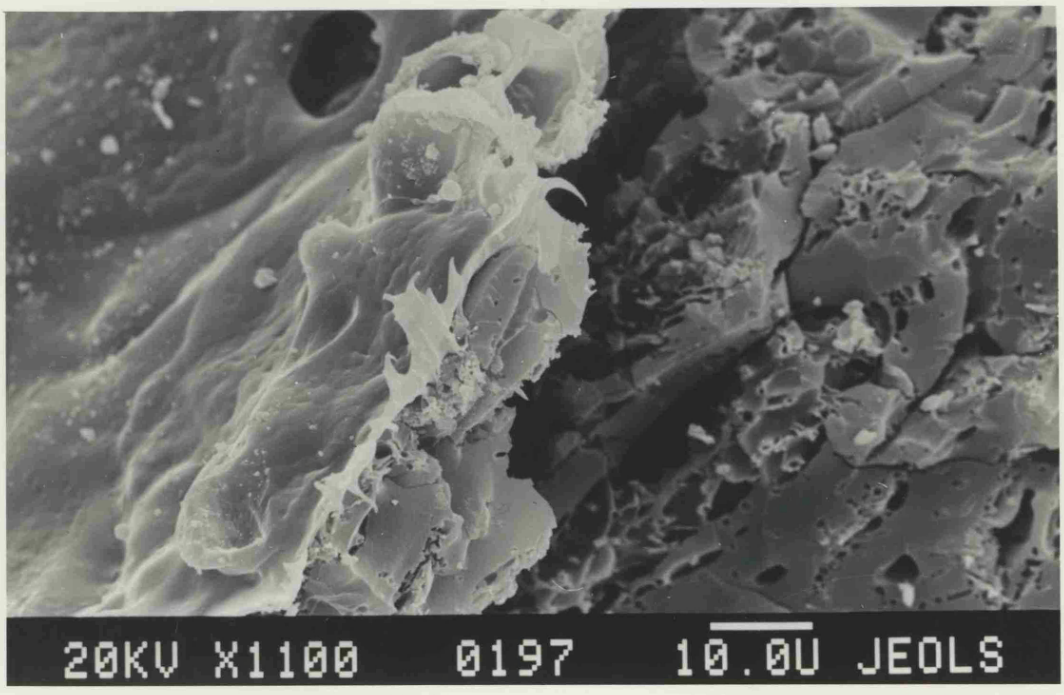


Plate 4.8 Transverse Fracture of Nylon 6 Coated Active Carbon x 2,800 Magnification.

(10 μm)

fusion systems in which the polymer coat is applied to increase the compatability of the sorbent with blood (Section 1.1.1). Sparks (1975) has suggested that the sorption capacity of the adsorbent for a specific molecule might be increased by the use of a selective polymeric microcapsule wall surrounding active carbon granules. No attempts have been made to resolve the function of the polymer coat and the carbon core in the overall sorption process or the affect that this may have on competitive rate and equilibrium interactions. The influence of a polymer coat on the sorption of a solute from solution by active carbon might be expected to be twofold. Firstly, the polymer coat may block some of the entrances to the internal pore network which may result in a lowering of the capacity of the sorbent for the solute. Secondly, the coating may affect the sorption properties of the core carbon by reducing the rate at which solute can interact with it. Equilibrium sorption isotherms for 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate from single solute solution (figures 3.23 to 3.25) show that the initial slopes of the isotherms are superimposable upon the uncoated ones and that suppression of uptake only arises at higher values of uptake. This is particularly well shown in the case of ethyl 4-aminobenzoate where the degree of suppression at high value is sufficient to change the isotherm type from L_1 to L_2 type (figure 3.25). These observations suggest that the interaction with the core carbon granule is essentially unaltered by the presence of the coat. The overall capacity is reduced which is probably due to a gross blockage of the entrances to a proportion of the internal pores. The data in tables 3.29 to 3.31 show that the Radke, Langmuir and Freundlich equations

do not fit the experimentally determined isotherms for the coated carbon sorbent. This probably arises from the nature of the isotherm where the initial slope does not significantly differ from the uncoated carbon isotherm whereas the change in isotherm slope in the region of the plateau is greater than with the uncoated sorbent which is probably due to pore entrance blockage.

The rate of sorption of a solute may also be altered by the rate at which is can permeate through the nylon 6 coat. The rate of permeation will be governed by the nylon 6 sorption K value and diffusion coefficient. Figure 3.52 shows that the rate of sorption of 4-nitrophenol on to the coated carbon is significantly slower than for the uncoated material. This was also found for the sorption kinetics of 4-methoxybenzoic acid and ethyl 4-aminobenzoate (figures 3.56). The effect of initial concentration on the rate of sorption of 4-nitrophenol was studied to characterise the nature of the kinetic profile arising from dynamic sorption on to nylon 6 coated active carbon. Figure 3.52 also shows that the shape of the kinetic profiles differ from those of the uncoated carbon as the three characteristic phases are less well defined over the 300 minute determination period. The linear $t^{\frac{1}{2}}$ plot region for the sorption of 4-nitrophenol is extended from 25 for the uncoated carbon to 225 minutes on the coated sorbent for the 10^{-3} M initial concentration system (figure 3.53). The duration of the linear $t^{\frac{1}{2}}$ region is however reduced from 225 to 56 minutes as the concentration increases from 10^{-3} M to $5x10^{-3}$ M. This would suggest that the carbon subspace is still a determinant of sorption rate although its role would appear to be substantially modified. The presence of the coat reduces the rate of uptake with respect to the uncoated material

indicating that the polymer is contributing to the overall control of the rate of sorption.

Preliminary studies showed that the degree of suppression arising from the presence of the coat was not constant throughout the period of the determination. Initially, the degree of suppression of the rate of uptake was low and increased as the elapsed time increased. Consideration of the relative rate constants would, not therefore be representative of the sorption process over the full 300 minute period. To assist in the visualisation of the effect of coating on the rate of sorption, a coating suppression factor, S^{ct}, may be used (equation 4.18).

$$S^{ct} = \frac{n^{ct}}{n} \quad \ldots\ldots\ldots (4.18)$$

where S^{ct} = the suppression factor at time. t.

n = the uptake from single solute solution on to active carbon at time, t.

n^{ct} = the uptake from single solute solution on to nylon 6 coated active carbon at time, t.

Values of S^{ct} were determined after 50, 100, 150, 200 and 250 minutes and these are summarised for the four initial concentrations of 4-nitrophenol studied in table 4.14.

Table 4.14 shows that the uptake is initially reduced by 50% and after 250 minutes is approximately 30% of the uptake of 4-nitrophenol on to the uncoated active carbon. The suppression factors for each concentration appear to be identical indicating that the percentage reduction in uptake due to the presence of the coat is not concentration dependent. The suppression factors for the other two model solutes are given in table 4.15, together with that for 4-

Table 4.14 Suppression Factors for the Effect of the Nylon 6 Coat in Suppressing the Rate of Uptake of 4-nitrophenol on to Active Carbon.

Initial Concentration	S^{ct}(mins)				
	50	100	150	200	250
1×10^{-3} M	0.56	0.53	0.40	0.35	0.31
2×10^{-3} M	0.52	0.40	0.34	0.30	0.26
3×10^{-3} M	0.50	0.40	0.35	0.32	0.27
4×10^{-3} M	0.50	0.39	0.35	0.31	0.29

Table 4.15 Suppression Factors for the Effect of the Nylon 6 Coat in Suppressing the Rate of Uptake of 4-nitrophenol, 4-methoxybenzoic acid and Ethyl 4-aminobenzoate (initial concentration 10^{-3} M.

Solute	S^{ct}(mins)				
	50	100	150	200	250
4-nitrophenol	0.55	0.47	0.40	0.35	0.31
4-methoxybenzoic acid	0.50	0.42	0.35	0.30	0.26
ethyl 4-aminobenzoate	0.57	0.46	0.40	0.37	0.33

nitrophenol.

The suppression factors for all three solutes and their time dependence appear to be similar, suggesting that the effect of the coat on rate suppression is apparently independent of the nature of these solutes.

Consideration of the permeability characteristics of the solutes through both nylon 6 and active carbon may support these findings. In the case of the sorption of solutes by nylon 6 powder the linear isotherms may be represented by a single sorption constant; the K value, which is an estimate of the Henry's law constant for sorption. The isotherms for active carbon are, however, non-linear and differ in nature to those for the nylon 6 interaction. The initial region of the L isotherm may be considered to be linear, obeying Henry's law for sorption which is reflected in the α constant of Radke's equation (Equation 1.26). It is therefore possible to determine estimates of the diffusion process for both sorbents. Although the mechanism of solute transfer is different in each case, the diffusion coefficient describes the mass transport as if the internal structure of each sorbent were similar. Finally, the permeability coefficient for transport in nylon 6 can be obtained from equation 1.24. Although the solute isotherms on active carbon are non-linear, it should be possible to define a permeability coefficient where Henry's law is obeyed using the following equation.

$$P_{HL} = \alpha \times \bar{D} \quad \ldots\ldots\ldots\ldots \quad (4.19).$$

where P_{HL} = the permeability coefficient for the carbon

α = the Radke isotherm α constant.

$\bar{D}$ = the average diffusion coefficient for the carbon.

Mass transfer data for the sorption of 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate are summarised in table 4.16.
The data in table 4.16 shows that the permeability coefficients for the solutes studied for mass transfer through the nylon 6 film are all of the same order of magnitude although small differences are apparent. This is also the case for the sorption of solutes into active carbon. As the permeability coefficients through the nylon 6 film are about 7 orders of magnitude lower than those for the active carbon in each case, the relative suppression of rate should be similar for all three solutes. This may explain the apparent independence of the coating suppression factor on the nature of the solute. The wide difference in the permeability coefficients between carbon and nylon 6 also accounts for the reduced rate of uptake observed experimentally. It is possible, therefore, that the rate of sorption of solutes on to polymer coated carbon sorbents may be predicted from a consideration of their permeability coefficients in the coat and core, and the factors which affect them.
If polymer coatings are to be used to alter the competitiveness of the solutes and give a kinetic advantage to one or other species a degree of selectivity must be imparted to the composite sorbent by the coat. The only way in which the coat is likely to do this is by a selective retardation of mass transfer. This will occur either due to a significant difference in the nylon 6 or active carbon permeability coefficients or their ratio. As these three parameters are not significantly different for the three solutes used in this study, it is not likely that any degree of selectivity will have been imparted by the nylon 6 coat. The dynamic and equilibrium

Table 4.16 Comparative Data for the Mass Transfer of the Model Solutes in to Active Carbon and Nylon 6 from Aqueous Solution pH 2.32 (0.5M ionic strength) and 30°.

Solute	Affinity Constant $1Kg^{-1}$		Diffusion Coefficient $m^2 sec^{-1}$		Permeability Coefficient $m^2 sec^{-1}$	
	Nylon 6	Active Carbon	Nylon 6	Active Carbon	Nylon 6	Active Carbon
4-nitrophenol	42.3	9231	1.09×10^{-13}	1.75×10^{-9}	4.95×10^{-12}	1.61×10^{-5}
4-methoxybenzoic acid	29.2	18075	0.90×10^{-13}	0.89×10^{-9}	3.57×10^{-12}	1.61×10^{-5}
ethyl 4-aminobenzoate	9.3	8665	0.86×10^{-13}	0.64×10^{-9}	0.77×10^{-12}	0.55×10^{-5}

sorption of 4-nitrophenol, 4-methoxybenzoic acid and ethyl 4-aminobenzoate were studied on nylon 6 coated active carbon from binary mixed solutions to test the prediction that no overall improvement in selectivity for the carbon would be achieved by application of the polymer coat.

The sorption isotherms for the uptake of the model solutes from binary solute solution are again suppressed with respect to the single solute isotherms. The pattern of uptake, although suppressed, is similar to that of the binary solute solution isotherms obtained for the interaction with the uncoated carbon. This is particularly well demonstrated by the S isotherm for the sorption of 4-methoxybenzoic acid in the presence of ethyl 4-aminobenzoate (figure 3.34). In contrast, the single point plots for the uptake of the constant initial concentration solute in the mixture differ from those obtained on the uncoated material. In all three binary solute solutions studied the data points fell on a line parallel to the abscissa, indicating that the concentration dependence of the competitive sorption process is eliminated (figures 3.33,3.37,3.41). It would appear, therefore, that the coating acts to enhance the competitiveness of the solute present in the higher concentration. The mechanism by which this occurs is not clear from the available data. One possible explanation is that the solute in the higher concentration will permeate through the polymer film more rapidly and establish a high concentration within the carbon core. The solute present in the lower concentration will permeate through the film more slowly, and as the competitiveness is effectively lowered with respect to that on the uncoated material a higher degree of suppression is encountered.

A reduction in the competitiveness of the solute present at the lower concentration will result in a reduction in the extent of suppression encountered by the higher concentration species. The figures presented in Section 3.4.5 indicate that the rates of sorption of the model solutes are suppressed, in the presence of one another, as is the case with the uncoated carbon. Suppression factors were calculated as before (Equation 4.18) and are given in table 4.17. Table 4.17 indicates that a similar pattern of suppression occurs for binary solute dynamic sorption on to nylon 6 coated active carbon as with the uncoated material. This is also illustrated in table 4.18 where the mean suppression factors for both sorbent materials are compared. Although a slight improvement in selectivity appears to occur with respect to 4-nitrophenol the overall degree of suppression appears unchanged on both sorbents. It is apparent, therefore, that as predicted, although the nylon 6 film coat alters the permeability characteristics of the carbon with respect to the three model solutes, it does not significantly affect the selectivity.

Table 4.17 Suppression Factors for the Suppression of the Rate of Sorption of the Model Solutes on to Nylon 6 Coated Carbon in the Presence of Competing Species.

Solute	Competitor	Initial Concentration Ratio	S(mins) 50	100	150	200	250	Mean
ethyl 4-aminobenzoate	4-nitrophenol	0.2	0.44	0.46	0.49	0.53	0.52	0.49
4-methoxybenzoic acid	4-nitrophenol	0.2	0.32	0.31	0.32	0.39	0.35	0.34
4-nitrophenol	ethyl 4-amino-benzoate	0.2	0.44	0.49	0.50	0.53	0.55	0.50
4-methoxybenzoic acid	ethyl 4-amino-benzoate	0.2	0.46	0.51	0.51	0.51	0.54	0.51
4-nitrophenol	ethyl 4-amino-benzoate	5.0	0.08	0.05	0.02	0.00	0.00	0.03
4-nitrophenol	4-methoxybenzoic acid	5.0	0.00	0.00	0.00	0.00	0.00	0.00
ethyl 4-aminobenzoate	4-nitrophenol	5.0	0.16	0.11	0.11	0.10	0.10	0.12
ethyl 4-aminobenzoate	4-methoxybenzoic acid	5.0	0.00	0.03	0.07	0.07	0.07	0.05

Table 4.18 Selectivity Indices and Suppression Factors for the Rate of Sorption of Model Solutes by Uncoated and Nylon 6 Coated Active Carbon.

Solute	Competitor	Initial Concentration Ratio	Solute Mean Suppression Factor	
			Uncoated	Coated
ethyl 4-aminobenzoate	4-nitrophenol	0.2	0.43	0.49
4-methoxybenzoic acid	4-nitrophenol	0.2	0.32	0.34
4-nitrophenol	ethyl 4-amino-benzoate	0.2	0.54	0.50
4-methoxybenzoic acid	ethyl 4-amino-benzoate	0.2	0.46	0.51
4-nitrophenol	ethyl 4-amino-benzoate	5.0	0.16	0.03
4-nitrophenol	4-methoxybenzoic acid	5.0	0.19	0.00
ethyl 4-aminobenzoate	4-nitrophenol	5.0	0.00	0.12
ethyl 4-aminobenzoate	4-methoxybenzoic	5.0	0.05	0.05

C O N C L U S I O N S and S U G G E S T I O N S

for

F U R T H E R W O R K

The interaction of the model solutes with nylon 6 revealed that phenolic compounds appear to bind in a different manner to the benzoic acid derivatives. The differences in the interaction behaviour are summarised in table C.1.

C.1 Comparison of the Interaction Behaviour of Benzoic Acid and Phenolic Derivatives and Nylon 6.

Characteristic	Benzoic Acid Derivatives	Phenolic Derivatives
Affinity with respect to solubility *	Normal *	High *
Inflexion in Van't Hoff Isochore	Present	Absent
Competitive Sorption	Not observed under specified experimental conditions	Present
Co-Plasticisation	Not observed under specified experimental conditions	Present

* As predicted from the log : log relationship between sorption K value and solubility (Richardson 1973).

The findings of this study confirm reports in the literature based on thin layer chromatography that phenols may bind specifically to amide groups in the nylon 6 matrix whereas benzoic acid derivatives can only form a weak association. Permeability and diffusion studies showed that although phenolic derivatives can plasticise nylon 6 the way in which solute transfers through the matrix is not affected i.e. permeability remains a product of the sorption and diffusion coefficients. It would be of interest to study the effect of increasing the concentration of diffusing solute within the nylon 6

matrix to assess whether plasticisation arises and whether it subsequently affects the rate of mass transfer. The coplasticisation effect noted at high binary solute solution concentration is also of interest and requires further study to fully characterise this phenomenon.

Sorption studies with active carbon indicated that both classes of solute interacted by a similar mechanism. The solutes appeared to diffuse into the pore structure of the carbon and adsorb on to pore walls. Competitive sorption occurred in all systems studied and application of dilute solution thermodynamics showed the interaction to be highly non-ideal with respect to dilute solution theory. It would appear that the model solutes interact strongly with the surface and one another in a mixed adsorbed phase. The resulting binary solute equilibria are therefore complex and difficult to predict from single solute solution adsorption considerations.

Two types of approach to the study of sorption kinetics with respect to the solute-carbon interaction are discernable from the literature. Firstly, the rate of uptake is considered to change as a function of the physical nature of the sorption system e.g. solute concentration, granule weight, granule particle size. Secondly, the mass transfer within the sorbent is considered to be of greater importance. Changes in the rate of uptake arising from altering the dimensions and nature of the sorption system appear to be accounted for provided that fundamental knowledge of the intra-sorbent mass transfer behaviour is known. This study has shown that by employing the conservation of diffusing mass equation, (which results in a numerical value of the diffusion coefficient) it appears

that regardless of the environmental conditions of the sorption system, mass transfer within the sorbent remains approximately constant. It is possible, therefore, that the determination of the diffusion coefficient for mass transfer in carbons is of greater use than exhaustive measurement of the kinetics of uptake under different experimental conditions. It was shown that both the affinity of the sorbent and the diffusivity of the solute contributed to the overall "permeability" of solutes through the carbon. It is, therefore, likely that competitive sorption processes affect both the extent and rate of solute uptake. Further work is necessary in this area to assess the extent to which competitive sorption or steric hinderance within pores influences the rate of sorption of solutes from binary mixed solution.

Sparks (1975) has suggested that competitive sorption processes may be influenced by coating active carbon with a selectively permeable polymeric microcapsule wall. It was further argued that the microcapsule wall permeability could be altered such that access to the carbon pores would be restricted to the solute which was the subject of interest. Were this the case, small quantities of drugs could be removed from complex biological fluids containing relatively higher concentrations of endogenous, adsorbable competing species. Studies by Sparks and his co-workers have suggested that the differential permeability of solutes within the polymeric capsule wall is the major determinant of selectivity. This study, however, focuses attention on the permeability characteristics of the carbon and the polymer as determinants of selectivity. It has also demonstrated that competitive sorption processes will affect selectivity as well as the presence of the coat.

The design of efficient sorbents for detoxification requires a knowledge of both the likely nature of competitive sorption and the extent to which the application of the coat modifies both single and binary solute interactions. Consideration of these various factors leads to an almost prohibitively complex model of dynamic sorption into composite adsorbents. This study, has, however, indicated that predictions can be made concerning the mass transfer characteristics of nylon 6 coated active carbon based on simple equilibrium and kinetic sorption studies. Further work is required in this area to enable quantitative prediction of mass transfer in composite adsorbents to be achieved. It would be necessary to study systems of different carbons with a given polymer and vice versa and also use model solutes of different molecular weight and affinity for both carbon and polymer. In this way different permutations and combinations of sorption, diffusion and permeability coefficients could be tested for their effect on the overall mass transfer characteristics of the composite sorbent.

This project has served to indicate the way in which more efficient clinical sorbents can be developed based on simple fundamental sorption studies. It also indicates that sorbent materials currently used in Pharmacy and Medicine may be less efficient than predicted from simple, single solute in-vitro studies.

Although film coating may be a possible method of improving the efficiency and selectivity of active carbon sorbents certain misconceptions about the mechanism of selectivity have prevailed.

Before solute mass transfer in polymer coated carbons can be fully optimised an accurate model of selectivity which includes competitive sorption has to be developed. The use of sorption constants and diffusion and permeability coefficients for drug-sorbent interactions may be useful in achieving this objective.

APPENDIX 1

A.1.1.1 Least Squares Linear Regresssion Analysis.

When a linear relationship is assumed to exist between two variables, it is usual to fit a straight line by least-squares regression analysis. The simplest statistical model for this type of analysis assumes that the independent variable X is known without error of measurement, and that the corresponding measured values of the dependent variable Y are scattered normally from their true values. Hence each value Y_i of the dependent variable is normally distributed about a mean.

The method of least squares obtains estimates of the intercept a, and the slope b, in the linear equation $Y = a + bX$ such that the sum of the squares of the deviations of the observation Y_i from their mean values $\alpha + \beta X_i$ is a minimum.

These values are

$$a = \frac{\sum Y_i - b \sum X_i}{n} \qquad \text{(A.1.1)}$$

$$= \bar{Y} - b\bar{X} \qquad \text{(A.1.2)}$$

$$b = \frac{n \sum X_i Y_i - \sum X_i \sum Y_i}{n \sum X_i^2 - (\sum X_i)^2} \qquad \text{(A.1.3)}$$

$$= \frac{\sum (X_i - \bar{X})(Y_i - \bar{Y})}{\sum (X_i - \bar{X})^2} \qquad \text{(A.1.4)}$$

where n is the number of points on the line.

Correlation Coefficient.

The correlation coefficient (r) is defined as:-

$$r = \frac{\sum (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{(X_i - \bar{X})^2 (Y_i - \bar{Y})^2}} \qquad (A.1.5)$$

To represent a linear relationship between two variables, X and Y, r must be $\pm$ unity. The calculated value of r is compared with the tabulated value at the 5% probability level for n-2 degrees of freedom, and if found to be greater than the tabulated value, the observations are considered to be linearly related.

A.1.1.3 Variance of the Slope (b).

This is termed S_b^2 and is given by the equation:-

$$S_b^2 = \frac{\sigma e^2}{\sum (X_i - \bar{X})^2} \qquad (A.1.6)$$

where σe^2 is the residual variance of the dependent variable Y and is obtained from:-

$$\sigma e^2 = \frac{\sum D^2}{n - 2} \qquad (A.1.7)$$

where $\sum D^2$ is the residual sum of squares.

$\sum D^2$ is obtained from the equation:-

$$\sum D^2 = (Y_i - \bar{Y})^2 - b^2 \sum (X_i - \bar{X})^2 \qquad (A.1.8)$$

The standard deviation of the slope is given by the square root of the variance.

Variance of the Intercept (a).

This is termed S_a^2 and is given by the equation:-

$$S_a^2 = \frac{\sum X_i^2 \cdot \sigma e^2}{n \cdot \sum (X_i - \bar{X})^2} \qquad \text{(A.1.9)}$$

where $$\sigma e^2 = \frac{\sum D^2}{n - 2} \qquad \text{(A.1.10)}$$

The standard deviation of the intercept is given by the square root of the variance.

To Determine the Equality of Two Estimates of a Parameter.

A.1.1.5 The test is generally known as the Student 't' test. The equality of estimates P_1 and P_2 with variance S_1^2 and S_2^2 respectively of a parameter P is assessed by means of the following statistic:-

$$t = \frac{P_1 - P_2}{\sqrt{S_1^2 + S_2^2}} \qquad \text{(A.1.11)}$$

The value of 't' is compared with tabulated values with $n_1 + n_2 - 4$ degree of freedom where n_1 and n_2 are the number of observations used in the estimation of P_1 and P_2 respectively. If the calculated value of 't' exceeds the tabulated value at the 5% probability level, the parameters are considered to be significantly different at that level.

A.1.1.6 To Determine the Equality of more than Two Estimates of a Parameter.

This is carried out using multiple linear regression and analysis of variance. The replicate experimental data were submitted to a multiple linear regression analysis using the statistical package MINITAB (Ryan, et al, 1981), using the following linear equation.

$$Y = a_1X_1 + b_1X_2 + a_2X_3 + b_2X_4 \quad \ldots\ldots\ldots\ldots \quad (A.1.12)$$

The analysis of variance of the linear regression gives a value for the residual sum of squares (RSS). The data is then pooled and resubmitted to the linear regression analysis (Section A,1,1) to obtain a value for the common slope. The value of residual sum of squares is then obtained as before (RSS'). The analysis proceeds by comparing the difference in the residual sum of squares between fits with a common and different slopes divided by the residual sum of squares. The F statistic is

$$(RSS' - RSS) / K - 1 \quad \ldots\ldots\ldots\ldots (A.1.13)$$

where K = the number of estimates of the parameter divided by

$$RSS / (n_K - 2_K) \quad \ldots\ldots\ldots\ldots (A.1.14)$$

where n_K = the total number of data points.

The test for significance involves comparing the calculated value of F with the tabulated value which has $K - 1$, $n_K - 2_K$ degrees of freedom. If the calculated value is less than the tabulated value for a specified level of significance then the

various estimates were considered to be not significantly different at that level.

A.1.2 Multiple Linear Regression.

This was carried out using the statistical package MINITAB (Ryan et al, 1981) which was available as a library routine on the Bath University Honeywell computer.

A.1.3 Non-Linear Regression.

The full mathematical and computational details of non-linear regression are presented in the manual to NONLIN, a computer package (Metzler, Metzler et al 1974). The NONLIN computer program was used in this study. The program linearises the non-linear equation using a Taylor series expansion using first derivative terms only. The series of equations arising from this treatment are solved by a multiple linear regression technique employing a singular value decomposition method to avoid problems associated with the inversion of frequently ill-conditioned matrices. The routine is iterative and so must be supplied with initial estimates of the non-linear equation constants. The program then utilises the experimental data, the equation which is supplied as an assignment statement in a fortran subroutine and the initial estimates of the equation constants. The program cycles, converging on a solution which produces a best fit set of constants for the model equation with respect to the experimental data. The program continues to fit the data until a specified limit of error is attained whereupon the results are listed.

A.1.4 To Determine the Equality of Two Means of a Parameter.

This is determined using the Two Tailed 't' Test Statistic:-

$$\frac{\bar{X}_1 - \bar{X}_2}{S\sqrt{\frac{1}{n_1} \quad \frac{1}{n_2}}} \qquad \text{(A.1.15)}$$

where $\bar{X}_1$ and $\bar{X}_2$ are the two means, n_1 and n_2 are the number of observations used in the estimation of $\bar{X}_1$ and $\bar{X}_2$. S represents the total standard deviation and is given by:-

$$S = \sqrt{\frac{(n_1 - 1)\ S_1^2 + (n_2 - 1)\ S_2^2}{(n_1 + n_2) - 2}} \qquad \text{(A.1.16)}$$

where S_1 and S_2 are the standard deviations associated with $\bar{X}_1$ and $\bar{X}_2$.

The value of 't' is compared with tabulated values with $n_1 + n_2 - 2$ degrees of freedom. If the calculated value of 't' exceeds the tabulated value at the 5% probability level, the means are considered to be significantly different at that level.

APPENDIX 2

EXPERIMENTAL DATA

Table A2.1 Data for the Adsorption of 4-methoxybenzoic acid on to Active Carbon at pH 2.32 (ionic strength 0.5M) and 30°C.

Initial Concentration M x 10^4	Equilibrium Concentration M x 10^4	Weight gramme	Uptake mol Kg^{-1}
1.586	0.208	0.0207	0.33
1.586	0.045	0.0214	0.77
3.205	0.248	0.0192	0.77
3.205	0.318	0.0198	0.73
4.718	0.664	0.0210	0.97
6.323	1.014	0.0211	1.26
7.251	1.279	0.0192	1.56
7.251	1.408	0.0198	1.47
9.495	2.072	0.0185	2.01
10.960	2.525	0.0200	2.11
10.960	2.611	0.0201	2.08
12.520	2.590	0.0211	2.35
12.520	3.453	0.0188	2.41
11.200	3.415	0.01521	2.56
11.200	3.431	0.0153	2.53
11.200	3.674	0.0146	2.58
11.200	3.884	0.0134	2.73
11.200	4.062	0.0124	2.87
11.200	4.597	0.0119	2.76
5.195	1.894	0.0103	1.60
7.461	2.671	0.0108	2.22
7.461	3.075	0.0100	2.20
8.756	3.464	0.0079	2.73

Table A2.2 Data for the Adsorption of 4-nitrophenol by Active Carbon at pH 2.32 (ionic strength 0.5M) and 30°.

Initial Concentration of 4-nitrophenol x 10^{3} M	Equilibrium Concentration of 4-nitrophenol x 10^{3} M	Weight of adsorbent gramme	Uptake $mol\ Kg^{-1}$
Determination I			
5.059	3.640	0.0184	3.85
5.059	3.498	0.0213	3.66
9.990	8.262	0.0215	4.03
9.990	8.262	0.0200	4.34
19.890	17.950	0.0204	4.76
19.890	18.080	0.0201	4.50
29.870	28.220	0.0183	4.50
29.870	28.220	0.0191	4.32
40.040	38.190	0.0206	4.36
40.040	38.190	0.0200	4.63

/continued...

Table A2.2 (Continued)

Initial Concentration of 4-nitrophenol x 10^3 M	Equilibrium Concentration of 4-nitrophenol x 10^3 M	Weight of adsorbent gramme	Uptake mol Kg^{-1}
Determination II			
0.133	0.050	0.0217	0.19
0.260	0.095	0.0204	0.40
0.522	0.153	0.0211	0.88
0.776	0.415	0.0181	0.99
0.991	0.445	0.0204	1.33
1.041	0.442	0.0182	1.65
2.006	1.068	0.0217	2.16
3.023	1.847	0.0195	3.01
3.961	2.503	0.0217	3.36
3.967	2.478	0.0231	3.22
4.965	3.381	0.0217	3.65
5.074	3.466	0.0219	3.85
Determination III			
0.133	0.500	0.0216	0.30
0.260	0.956	0.0199	0.45
0.522	0.153	0.0196	1.07
0.627	0.271	0.0202	0.88
0.627	0.248	0.0207	0.92
0.776	0.212	0.0205	1.38
1.256	0.636	0.0200	1.59
1.256	0.575	0.0201	1.69
1.884	0.929	0.0224	2.13
1.884	0.938	0.0233	2.03
2.534	1.312	0.0240	2.60
2.534	1.363	0.0204	2.87
3.170	1.888	0.0230	2.79
3.792	2.379	0.0197	3.58

Table A2.3 Data for the Adsorption of Ethyl 4-aminobenzoate by Active Carbon at pH 2.32 (0.5M ionic strength) and 30°.

Initial Concentration M x 10^4	Equilibrium Concentration M x 10^4	Weight gramme	Uptake mol Kg^{-1}
1.24	0.16	0.0217	0.25
1.24	0.20	0.0198	0.26
2.45	0.45	0.0221	0.45
2.45	0.78	0.0169	0.49
3.68	0.99	0.0216	0.62
3.68	1.37	0.0168	0.69
4.90	1.58	0.0203	0.82
6.17	1.89	0.0194	1.10
6.17	1.58	0.0199	1.16
7.39	2.73	0.0201	1.16
7.39	2.70	0.0213	1.10
8.65	4.12	0.0189	1.20
8.65	3.62	0.0203	1.24
9.25	3.73	0.0194	1.42
9.25	4,82	0.0168	1.32
18.47	9.43	0.0225	2.01
27.81	17.35	0.0207	2.53
27.81	17.75	0.0202	2.49
37.08	25.23	0.0226	2.62
46.36	33.06	0.0222	3.00
46.36	33.83	0.0213	2.94
55.90	42.41	0.0195	3.51
55.90	42.70	0.0188	3.46
64.78	50.75	0.0212	3.31
71.28	59.02	0.0163	3.76
71.28	57.80	0.0192	3.51
74.16	60.87	0.0195	3.40

Table A2.4 Data for the Adsorption of Phenol on to Active Carbon at pH 2.32 (ionic strength 0.5M) and 30°.

Initial Concentration $M \times 10^3$	Equilibrium Concentration $M \times 10^3$	Weight gramme	Uptake mol Kg^{-1}
1.037	0.746	0.0191	0.77
1.576	1.181	0.0197	1.00
2.576	2.056	0.0194	1.34
3.111	2.447	0.0215	1.54
4.135	3.437	0.0182	1.92
4.670	3.809	0.0217	1.99
5.145	4.345	0.0196	2.05
5.145	4.277	0.0206	2.10
0.628	0.448	0.0202	0.45
0.628	0.457	0.0192	0.45
1.261	0.935	0.0212	0.77
1.261	0.911	0.0215	0.82
1.901	1.478	0.0221	0.96
1.901	1.440	0.0214	1.08
2.512	1.984	0.0193	1.37
2.512	1.997	0.0203	1.27
3.152	2.542	0.0204	1.50
3.152	2.519	0.0203	1.56
3.790	2.988	0.0231	1.74
3.790	3.084	0.0205	1.75
4.457	3.753	0.0193	1.83
4.457	3.703	0.0191	1.97
5.075	4.397	0.0176	1.93
5.075	4.211	0.0210	2.06

Table A2.5 Data for the Adsorption of 4-methoxybenzoic acid on to Nylon 6 Coated Active Carbon at pH 2.32 (ionic strength 0.5M) and 30°.

Initial Concentration M x 10^4	Equilibrium Concentration M x 10^4	Adsorbent weight gramme	Uptake mol Kg^{-1}
1.261	0.267	0.0106	0.47
1.261	0.378	0.0086	0.71
2.492	0.405	0.0106	0.99
2.492	0.505	0.0108	0.92
3.742	1.754	0.0090	1.11
3.742	1.360	0.0100	1.19
4.993	2.331	0.0082	1.62
4.993	1.869	0.0113	1.38
6.328	3.399	0.010	2.03
6.328	2.929	0.016	1.89
7.591	3.415	0.010	2.09
7.591	3.852	0.0089	2.18
8.772	4.855	0.0092	2.13
8.772	4.321	0.0098	2.28
10.100	6.308	0.0100	2.55
10.100	5.212	0.0092	2.65

Table A2.6 Data for the Adsorption of 4-nitrophenol on to Nylon 6 Coated Active Carbon at pH 2.32 (ionic strength 0.5M) and 30°.

Initial Concentration $M \times 10^3$	Equilibrium Concentration $M \times 10^3$	Weight gramme	Uptake mol Kg^{-1}
0.613	0.155	0.0210	1.09
0.613	0.241	0.0160	1.16
1.246	0.478	0.0205	1.87
1.246	0.577	0.0190	1.76
1.843	1.080	0.0186	2.05
1.843	0.953	0.0209	2.12
2.486	1.510	0.0187	2.62
2.486	1.439	0.0208	2.52
3.095	1.951	0.0219	2.61
3.095	2.078	0.0196	2.59
3.686	2.726	0.0195	2.47
3.686	2.478	0.0213	2.84
4.347	3.084	0.0200	3.16
4.347	3.050	0.0216	3.00
4.940	3.593	0.0209	3.23
9.946	8.516	0.0194	3.68
9.946	8.325	0.0209	3.89
19.890	18.300	0.0202	3.94
19.890	18.370	0.0207	3.67
29.870	28.220	0.0203	4.06
29.870	28.210	0.0201	4.13
40.040	38.260	0.0191	4.66
40.040	38.260	0.0205	4.35
50.080	48.230	0.0196	4.72

Table A2.7 Data for the Adsorption of Ethyl 4-aminobenzoate on to Nylon 6 Coated Active Carbon at pH 2.32 (ionic strength 0.5M) and 30°.

Initial Concentration $M \times 10^3$	Equilibrium Concentration $M \times 10^3$	Adsorbent weight gramme	Uptake mol Kg^{-1}
0.796	0.242	0.0230	1.20
0.796	0.246	0.0240	1.15
1.633	1.037	0.0196	1.52
1.633	0.972	0.0189	1.75
2.414	1.665	0.0190	1.97
2.414	1.591	0.0204	2.02
3.260	2.441	0.0209	1.96
3.260	2.335	0.0222	2.08
4.045	3.174	0.0198	2.20
4.045	3.171	0.0208	2.10
4.912	3.943	0.0218	2.22
4.912	3.931	0.0222	2.21
5.783	4.880	0.0207	2.18
6.627	5.686	0.0216	2.28
6.627	5.686	0.0214	2.20

Table A2.8 Data for the Adsorption and Desorption Single Point Uptake Values for the Four Model Solutes at pH 2.32 (0.5M ionic strength) and 30°C on to Active Carbon.

Compound	Initial Concentration	Adsorption Equilibrium Concentration M x10^{3}	Desorption Equilibrium Concentration Mx10^{3}	Weight of Adsorbent gramme	Uptake(Ads) mol Kg^{-1}	Uptake(Des) mol Kg^{-1}
Phenol	5.024	4.264	2.637	0.0211	1.81	1.62
		4.285	2.705	0.0189	1.96	1.60
		4.224	2.637	0.0228	1.75	1.53
		4.312	2.678	0.0197	1.81	1.58
4 nitro-phenol	4.952	3.532	2.128	0.0214	3.31	2.59
		3.529	2.125	0.0214	3.30	2.58
		3.528	2.196	0.0216	3.29	2.61
		3.528	2.217	0.0209	3.41	2.67
ethyl 4-amino-benzoate	7.429	5.806	3.528	0.0231	3.51	3.42
		5.852	3.573	0.0219	3.60	3.46
		6.240	3.514	0.0194	3.06	3.65
		5.811	3.541	0.0226	3.57	3.45
4 methoxy-benzoic acid	1.020	0.219	0.191	0.0195	2.06	1.93
		0.212	0.192	0.0203	1.99	1.83
		0.210	0.191	0.0209	1.94	1.78
		0.238	0.190	0.0188	2.08	1.96

Table A2.9 Data for the Absorption of 4-nitrophenol and Phenol from Binary Mixed Solution on to Active Carbon at pH 2.32 (0.5M ionic strength) and 30°.

Initial Concentration $\times 10^{3}$ M		Equilibrium Concentration $\times 10^{3}$ M		Weight gramme	Uptake mol Kg^{-1}	
4-nitrophenol	phenol	4-nitrophenol	phenol		4-nitrophenol	phenol
0.126	5.106	0.034	4.316	0.0224	0.21	1.76
0.126	5.106	0.020	4.067	0.0291	0.13	1.79
0.252	5.125	0.070	4.494	0.0184	0.49	1.71
0.252	5.125	0.058	4.351	0.0208	0.47	1.86
0.377	5.098	0.106	4.478	0.0190	0.72	1.63
0.377	5.098	0.104	4.521	0.0182	0.75	1.58
0.502	5.128	0.159	4.601	0.0178	0.97	1.48
0.502	5.128	0.172	4.504	0.0199	0.83	1.57
0.628	5.098	0.217	4.496	0.0216	0.95	1.39
0.628	5.098	0.191	4.489	0.0211	1.09	1.45
0.750	5.141	0.264	4.605	0.0184	1.32	1.46
0.750	5.141	0.266	4.636	0.0178	1.36	1.42
0.873	5.145	0.307	4.622	0.0193	1.47	1.36
0.873	5.145	0.447	4.718	0.0193	1.11	1.11
0.993	5.093	0.431	4.700	0.0181	1.56	1.08
0.993	5.093	0.431	0.577	0.0214	1.31	1.02
0.985	1.605	0.349	1.333	0.0223	1.42	0.61
0.985	1.605	0.368	1.358	0.0186	1.66	0.67
0.988	2.130	0.412	1.805	0.0208	1.39	0.78
0.988	2.130	0.320	1.798	0.0220	1.52	0.76
0.986	2.562	0.380	2.288	0.0190	1.60	0.72
0.983	2.562	0.403	2.277	0.0210	1.39	0.68
0.988	3.102	0.356	2.688	0.0203	1.56	1.02
0.988	3.102	0.431	2.780	0.0168	1.66	0.96
0.990	3.642	0.336	3.343	0.0190	1.71	0.78
0.990	3.642	0.380	3.270	0.0183	1.67	1.02
0.974	4.098	0.486	3.657	0.0189	1.29	1.17
0.980	4.098	0.486	3.708	0.0190	1.30	1.03
0.988	4.570	0.354	4.080	0.0220	1.44	1.11
0.990	5.143	0.351	4.628	0.0201	1.59	1.28
0.990	5.143	0.364	4.697	0.0186	1.68	1.20
2.987	1.810	1.804	1.666	0.0194	3.05	0.37
2.987	1.810	1.805	1.595	0.0194	3.04	0.55
3.040	2.323	1.805	2.131	0.0195	3.17	0.49
3.019	2.800	1.801	2.168	0.0198	3.08	0.46
3.019	2.800	1.750	2.561	0.0199	3.19	0.60
2.992	3.355	1.734	3.099	0.0201	3.13	0.64
2.992	3.849	1.716	3.578	0.0211	3.02	0.64
2.992	3.849	1.716	3.549	0.0199	3.20	0.75

Table A2.9 / Continued.

Initial Concentration $\times 10^{3}$ M		Equilibrium Concentration $\times 10^{3}$ M		Weight gramme	Uptake mol Kg^{-1}	
4-nitrophenol	phenol	4-nitrophenol	phenol		4-nitrophenol	phenol
2.992	4.344	1.758	4.044	0.0202	3.05	0.74
2.992	4.344	1.800	4.059	0.0197	3.02	0.72
2.992	4.944	1.802	4.604	0.0184	3.23	0.92
2.987	5.375	1.802	5.067	0.0190	3.12	0.81
4.978	1.820	3.666	1.703	0.0177	3.71	0.33
4.978	1.820	3.587	1.721	0.0209	3.33	0.24
4.964	2.320	3.702	2.163	0.0198	3.19	0.40
4.964	2.320	3.713	2.138	0.0184	3.40	0.49
4.964	2.896	3.609	2.713	0.0190	3.57	0.48
4.964	2.896	3.632	2.701	0.0203	3.28	0.48
4.964	3.356	3.721	3.166	0.0183	3.40	0.52
4.964	3.356	3.723	3.116	0.0183	3.01	0.60
4.971	4.029	3.616	3.745	0.0202	3.35	0.70
4.971	4.029	3.632	3.792	0.0194	3.45	0.61
4.971	4.500	3.683	4.311	0.0192	3.35	0.49
4.971	4.500	3.632	4.357	0.0192	3.49	0.37
4.964	4.938	3.553	4.789	0.0186	3.79	0.40
4.964	4.938	3.576	4.690	0.0204	3.40	0.61
4.964	5.381	3.914	5.184	0.0187	2.81	0.53
4.964	5.381	3.637	5.139	0.0212	3.14	0.57

Table A2.10 Data for the Adsorption of 4-methoxybenzoic acid and 4-nitrophenol from Binary Mixed Solution at pH 2.32 (ionic strength 0.5M) and 30° on to Active Carbon.

Initial Concentration		Equilibrium Concentration		Weight (g)	Uptake mol Kg^{-1}	
4-nitrophenol $\times 10^{3}$ M	4-methoxybenzoic acid $\times 10^{3}$ M	4-nitrophenol $\times 10^{3}$ M	4-methoxybenzoic acid $\times 10^{4}$ M		4-nitrophenol	4-methoxybenzoic acid
3.015	1.315	1.782	0.489	0.0198	3.11	0.21
3.015	1.315	1.650	0.403	0.0232	2.94	0.20
2.979	2.524	1.834	0.854	0.0199	2.81	0.42
2.979	2.524	1.834	0.894	0.0205	2.79	0.40
2.949	3.817	2.082	1.612	0.0162	2.68	0.68
2.949	3.817	1.751	1.176	0.0216	2.77	0.61
2.995	5.004	1.927	1.940	0.0205	2.60	0.75
2.995	5.004	2.003	1.952	0.0195	2.53	0.78
2.995	6.315	2.003	2.360	0.0195	2.54	1.01
2.995	6.315	2.237	3.299	0.0160	2.37	0.94
3.010	7.614	1.891	2.478	0.0220	2.54	1.17
3.010	7.614	2.039	3.045	0.0203	2.39	1.12
3.000	8.852	2.135	3.991	0.0183	2.36	1.33
3.000	8.852	2.140	3.988	0.0188	2.29	1.30
3.045	9.854	2.039	4.615	0.0218	2.31	1.20
3.045	9.854	2.186	4.795	0.0188	2.28	1.34
4.972	1.347	3.549	0.698	0.0210	3.39	0.16
4.972	1.347	3.528	0.682	0.0195	3.70	0.17
4.962	2.649	3.610	1.429	0.0196	3.45	0.31
4.962	2.649	3.640	1.487	0.0193	3.43	0.30
5.023	3.881	3.711	2.193	0.0205	3.20	0.41
5.023	3.881	3.640	2.085	0.0192	3.60	0.47

/ Continued

Table A2.10 / Continued

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
4-nitrophenol $\times 10^{3}$ M	4-methoxy-benzoic acid $\times 10^{3}$ M	4-nitrophenol $\times 10^{3}$ M	4-methoxy-benzoic acid $\times 10^{4}$ M		4-nitrophenol	4-methoxy-benzoic acid
5.064	5.097	3 549	2 575	0 0210	3 61	0 60
5.064	5 097	3 803	2.738	0.0213	2.97	0 56
4 982	6.389	3 793	3 911	0 0203	2 93	0 61
4 982	6.389	3 620	3 654	0.0192	3 55	0.71
5.054	7 694	3 813	4.657	0 0195	3.18	0 78
5 054	7 694	3 813	4 495	0.0188	3.30	0 84
4 956	8.950	3 854	5 613	0.0189	2.90	0 88
4.956	8.950	3.620	5 742	0.0209	3 20	0 77
4 955	10.340	3 796	6 304	0.0201	2 88	1.00
4 955	10.340	3 898	6 485	0.0194	2.72	0.99
1 010	1 319	2.504	0 157	0 0215	1 76	0 27
1 010	1.319	2 822	0.141	0.0195	1 87	0.30
0.998	2.551	4 271	0 889	0 0211	1 35	0 39
0 998	2 551	3.788	0 748	0 0210	1 48	0 43
0.998	3.813	4 296	1 219	0 0192	1 48	0 68
0 998	3.813	4 233	1 224	0 0220	1 30	0 59
1 017	5.126	4 754	1 904	0 0185	1 46	0 87
1 017	5.126	4 220	1 597	0 0211	0.76	0.84
1 012	6 352	4 855	2 350	0.0204	1.29	0 98
1 012	6 352	4 932	2 376	0 0196	1 33	1 02

/ Continued..

Table A2.10 / Continued

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
4-nitrophenol $\times 10^{3}$ M	4-methoxy-benzoic acid $\times 10^{3}$ M	4-nitrophenol $\times 10^{3}$ M	4-methoxy-benzoic acid $\times 10^{4}$ M		4-nitrophenol	4-methoxy-benzoic acid
1 024	7.766	4 728	2.813	0.0229	1 20	1.08
1.024	7.766	4 754	2 811	0 0174	1.58	1 42
1 012	8.795	4 881	3.367	0.0214	1 23	1.27
1.012	8.795	5 593	3.880	0.0187	1.21	1 31
1 019	10.070	5.389	4 298	0 0209	1.15	1.38
1 019	10.070	4 728	3.476	0.0239	1.14	1.38

Table A2.11 Data for the Adsorption of 4-methoxybenzoic acid and Ethyl 4-aminobenzoate on to Active Carbon from Binary Mixed Solution at pH 2.32 (ionic strength 0.5M) and 30°.

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
ethyl 4-aminobenzoate $M \times 10^{3}$	4-methoxy-benzoic acid $M \times 10^{4}$	ethyl 4-aminobenzoate $M \times 10^{3}$	4-methoxy-benzoic acid $M \times 10^{4}$		ethyl 4-aminobenzoate	4-methoxy-benzoic acid
2.957	1.688	1.845	1.167	0.0214	2.59	0 12
2.957	1.688	1.949	1.303	0.0210	2.40	0 09
2.945	2.832	1.915	1.643	0.0215	2.40	0.28
2.945	2.832	1.851	1 901	0.0222	2 47	0 21
2.943	3.957	2.000	2 891	0.0193	2.44	0 28
2.943	3.957	1.797	2 311	0 0201	2 78	0 40
2.942	5.205	1.945	3.401	0 0203	2.45	0 44
2.942	5.205	1.923	3.249	0.0202	2.52	0 48
2.974	6.782	2.033	4.119	0 0200	2.34	0 67
2.974	6.782	1.998	4.190	0.0190	2.57	0.68
2.984	7.958	2.216	5 439	0 0190	2.01	0 66
2.984	7.958	2.010	5.139	0.0221	2.20	0 64
2.958	0.054	2.054	5.670	0.0193	2.34	0 82
2.958	9.054	2.138	5 897	0.0209	1.97	0 76
2.958	9.654	2.037	6.251	0.0206	2 24	0 84
2.958	9.654	2.023	5 883	0 0201	2 32	0 94
4.843	2.184	3.535	1.491	0 0183	3.57	0 19
4.843	2.184	3.535	1.585	0.0209	3 13	0.14
4.843	2.803	3.553	2.423	0 0216	2.99	0.09
4.843	2.803	3.178	2.090	0.0262	3.18	0.14

Continued / .....

Table A2.11 Continued

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
ethyl 4-aminobenzoate $M \times 10^{3}$	4 methoxy-benzoic acid $M \times 10^{4}$	ethyl 4-aminobenzoate $M \times 10^{3}$	4 methoxy-benzoic acid $M \times 10^{4}$		ethyl 4-aminobenzoate	4 methoxy-benzoic acid
4.855	4.104	3.594	3.235	0.0191	3.30	0.23
4.855	4.104	3.600	3.189	0.0193	3.25	0.24
4.835	5.450	3.540	3.707	0.0215	3.02	0.41
4.906	6.615	3.774	5.035	0.0217	2.61	0.36
4.904	7.740	3.819	5.915	0.0207	2.70	0.46
4.904	7.740	3.808	5.755	0.0207	2.65	0.48
4.902	9.050	4.015	6.340	0.0203	2.19	0.67
4.902	9.050	3.819	6.405	0.0201	2.69	0.66
5.015	10.03	4.026	6.765	0.0195	2.54	0.84
5.015	10.03	3.961	6.560	0.0206	2.56	0.84

/ Continued...

Table A2.11 Continued

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
ethyl 4-aminobenzoate M x 10^4	4-methoxy-benzoic acid M x 10^4	ethyl 4-aminobenzoate M x 10^4	4-methoxy-benzoic acid M x 10^4		ethyl 4-aminobenzoate	4-methoxy-benzoic acid
9.648	1.543	3.679	0.501	0.0192	1.55	0.27
9.648	1.543	3.528	0.457	0.0191	1.60	0.28
9.658	2.755	3.811	0.800	0.0188	1.56	0.52
9.658	2.755	3.494	0.763	0.0186	1.66	0.53
9.610	3.998	4.253	1.261	0.0193	1.39	0.71
9.610	3.998	3.871	1.115	0.0124	1.28	0.64
9.693	5.213	3.833	1.348	0.0201	1.46	0.96
9.693	5.213	4.879	1.909	0.0203	1.19	0.81
9.743	6.583	4.486	2.054	0.0192	1.37	1.18
9.698	7.675	4.590	2.341	0.0195	1.31	1.31
9.698	7.675	4.239	2.170	0.0211	1.29	1.30
9.823	8.995	4.466	2.908	0.0201	1.33	1.51
9.823	8.995	5.261	3.353	0.0203	1.12	1.39
9.805	10.160	4.510	2.861	0.0188	1.41	1.94
9.805	10.160	5.325	3.871	0.0201	1.11	1.56

Table A2.12 Data for the Adsorption of 4-nitrophenol and Ethyl 4-aminobenzoate Active Carbon from Binary Mixed Solution at pH2.32 (ionic strength 0.5M) and 30°.

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
ethyl 4-amino-benzoate $M \times 10^3$	4-nitrophenol $M \times 10^3$	ethyl 4-amino-benzoate $M \times 10^3$	4-nitrophenol $M \times 10^3$		ethyl 4-amino-benzoate	4-nitrophenol
3.022	0.633	1.939	0.238	0.0211	2.69	0.94
3.022	0.633	2.015	0.252	0.0206	2.44	0.92
3.031	1.058	2.087	0.581	0.0199	2.37	1.20
3.031	1.058	2.142	0.594	0.0193	2.30	1.20
3.006	1.611	2.074	0.894	0.0217	2.14	1.65
3.006	1.611	2.108	1.001	0.0195	2.30	1.56
2.995	2.125	2.103	1.260	0.0215	2.07	2.01
2.995	2.115	2.363	1.383	0.0200	1.58	1.86
3.015	2.592	2.297	1.742	0.0200	1.79	2.12
3.015	2.592	2.175	1.702	0.0192	2.19	2.32
3.022	3.079	2.395	2.208	0.0213	1.47	2.04
3.022	3.079	2.155	1.996	0.0208	2.09	2.61
3.052	3.459	2.464	2.409	0.0189	1.56	2.78
3.052	3.459	2.437	2.402	0.0206	1.50	2.57
3.014	3.957	2.443	2.706	0.0197	1.45	3.17
3.014	3.957	2.472	2.758	0.0200	1.36	3.00
5.158	0.511	4.060	0.304	0.0216	2.54	0.48
5.158	0.511	4.058	0.290	0.0199	2.76	0.56
5.158	0.985	3.959	0.623	0.0229	2.62	0.79
5.158	0.985	4.182	0.673	0.0200	2.44	0.78

Table A2.12 Continued.

Initial Concentration		Equilibrium Concentration		Weight(g)	Uptake mol Kg^{-1}	
ethyl 4-amino-benzoate $M \times 10^3$	4-nitrophenol $M \times 10^3$	ethyl 4-amino-benzoate $M \times 10^3$	4-nitrophenol $M \times 10^3$		ethyl 4-amino-benzoate	4-nitrophenol
5.117	1.472	4.116	0.978	0.0218	2.29	0.88
5.117	1.472	4.102	1.079	0.0207	2.45	0.95
5.161	1.951	4.632	1.557	0.0210	1.26	1.07
5.161	1.951	4.287	1.452	0.10187	2.33	1.33
5.178	2.458	4.178	1.825	0.0221	2.26	1.43
5.178	2.458	4.208	1.924	0.0193	2.51	1.38
5.159	2.926	4.415	2.297	0.0198	1.88	1.59
5.116	3.438	4.273	2.614	0.0211	1.99	1.95
5.116	3.438	4.251	2.591	0.0220	1.97	1.93
5.174	3.934	4.433	3.092	0.0203	1.83	2.07
5.174	3.934	4.413	3.060	0.0198	1.92	2.21

Table A2.13 Date for the Adsorption of 4-methoxybenzoic acid and 4-nitrophenol on to Nylon 6 Coated Active Carbon from Binary Solute Solution at pH 2.32 (0.5M ionic strength) and 30°.

Initial Concentration		Equilibrium Concentration		Adsorbent weight(g)	Uptake mol Kg^{-1}	
4-methoxy-benzoic acid x 10^4 M	4-nitrophenol x 10^3 M	4-methoxybenzoic acid x 10^4	4-nitrophenol x 10^3 M		4-methoxy-benzoic acid	4-nitrophenol
1.49	4.99	0.84	3.97	0.0213	0.15	2.41
1.49	4.99	0.78	3.99	0.0206	0.17	2.35
2.59	4.93	1.52	4.03	0.0197	0.27	2.30
2.59	4.93	1.44	3.92	0.0208	0.28	2.44
4.01	4.96	2.20	3.96	0.0210	0.43	2.40
4.01	4.96	2.30	4.02	0.0189	0.45	2.51
5.37	4.99	2.61	3.85	0.0194	0.71	2.93
5.37	4.99	2.85	3.86	0.0216	0.59	2.62
6.54	4.97	3.74	4.11	0.0182	0.77	2.42
6.54	4.99	3.12	3.84	0.0224	0.76	2.57
7.96	5.03	5.16	4.07	0.0198	0.71	2.44
7.96	5.03	4.13	3.94	0.0202	0.95	2.72
9.26	5.07	5.79	4.08	0.0225	0.77	2.22
9.26	5.07	5.41	4.12	0.0189	1.02	2.54
10.490	4.95	5.90	3.90	0.0232	0.99	2.25
10.490	4.95	6.23	3.95	0.0220	0.97	2.27

Table A2.14 Data for the Adsorption of 4 nitrophenol and Ethyl 4 aminobenzoate on to Nylon 6 Coated Active Carbon from Binary Solute Solution at pH2.32 (0.5M ionic strength) and 30°.

Initial Concentration		Equilibrium Concentration		Adsorbent weight (g)	Uptake mol Kg^{-1}	
4-nitrophenol $M \times 10^3$	ethyl 4-amino-benzoate $\times 10^3$ M	4-nitrophenol $\times 10^3$ M	ethyl 4-amino-benzoate $\times 10^3$ M		4-nitrophenol	ethyl 4-amino-benzoate
0.483	5.431	0.30	4.60	0.0213	0.42	1.95
0 483	5.431	0.30	4.57	0.0218	0.41	1 96
0.982	5.461	0.65	4.56	0.0208	0.81	2 15
0.982	5.461	0.66	4.58	0.0211	0.76	2.10
1 491	5.552	1.08	4 .67	0.0216	0.92	2.04
1.491	5.552	1.12	4.76	0.0212	0.86	1 87
1.981	5.420	1.53	4.58	0.0204	1.11	2.06
1.981	5.420	1.45	4.56	0.0211	1.24	2.04
2.492	5.442	1.90	4.60	0.0196	1.50	2.13
2.492	5.442	1.92	4.68	0.0194	1.47	1.95
2.950	5.491	2.36	4.67	0.0201	1.46	2.05
2.950	5.491	2.35	4.61	0.0192	1.56	2.31
3.413	5.491	2.80	4.66	0.0195	1 58	2.13
3.413	5.491	2.80	4.69	0.0205	1.50	1 94
3 901	5.432	3.21	5.00	0.0201	1.72	1.08
3 901	5.432	3.22	4.78	0.0195	1.75	1.69

Table A2.15 The Effect of Stirring Rate on the Kinetics of Uptake of 4-nitrophenol on to 20 gramme of Active Carbon at pH 2.32 (ionic strength 0.5M) and 30° from 1000ml of 9.99×10^{-4}M Adsorbate Solution.

Shaft Speed RPM	Adsorbent weight(g)	Time (Min)	√Time √(Min)	Residual Concentration	Uptake$_{-1}$ mol Kg
700	2.001	1	1.0	9.43	2.79
		2	1.4	9.08	4.57
		4	2.0	8.29	8.51
		6	2.4	7.70	11.43
		9	3.0	7.00	14.92
		16	4.0	5.74	21.26
		22	4.7	4.95	25.18
800	2.002	4	2.0	8.29	8.49
		9	3.0	6.67	16.54
		13	3.6	5.83	20.72
		16	4.0	5.32	23.29
		20	4.5	4.79	25.91
		25	5.0	4.21	28.82
900	2.000	1	1.0	9.48	2.54
		2	1.4	9.02	4.83
		4	2.0	8.19	9.03
		6	2.4	7.49	12.52
		9	3.0	6.72	16.33
		16	4.0	5.41	22.91
		22	4.7	4.63	26.82
1000	2.000	1	1.0	9.41	2.92
		2	1.4	8.97	5.08
		4	2.0	8.11	9.40
		6	2.4	7.46	12.64
		9	3.0	6.60	16.96
		16	4.0	5.25	23.70
		22	4.7	4.37	28.08
900	2.001	1	1.0	9.48	2.03
		2	1.4	8.92	4.83
		4	2.0	8.10	8.96
		6	2.4	1.59	11.50
		9	3.0	6.72	15.82
		16	4.0	5.43	22.28
		22	4.7	4.58	26.55
1000	2.003	2	1.4	8.92	4.82
		3	1.7	8.52	6.86
		4	2.0	8.10	8.95
		6	2.4	7.46	12.12
		9	3.0	6.70	15.93
		13	3.6	5.28	23.03
		18	4.2	5.02	24.29

Table A2.16 The Rate of Uptake Data for 4-nitrophenol on to 1.0 gramme of Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30° at Various Initial Concentrations.

Time (min)	$Time^{\frac{1}{2}}_{\frac{1}{2}}$ ($min^{\frac{1}{2}}$)	Concentration $\times 10^{4}$ M	Uptake mol Kg^{-1}	Time (min)	$Time^{\frac{1}{2}}_{\frac{1}{2}}$ ($min^{\frac{1}{2}}$)	Concentration $\times 10^{3}$ M	Uptake mol Kg^{-1}
Initial Concentration 1.004×10^{-3} M				Initial Concentration 2.003×10^{-3} M			
2.0	1.4	9.393	0.065	2.0	1.4	1.876	0.127
5.0	2.2	8.757	0.133	5.0	2.2	1.779	0.223
6.0	2.4	8.503	0.154	6.0	2.4	1.749	0.254
8.0	2.8	8.109	0.193	8.0	2.8	1.701	0.302
10.0	3.2	7.868	0.202	10.0	3.2	1.640	0.362
12.0	3.5	7.524	0.251	12.0	3.5	1.589	0.414
15.0	3.9	7.232	0.265	15.0	3.9	1.538	0.464
18.0	4.2	6.749	0.329	18.0	4.2	1.474	0.528
22.0	4.7	6.355	0.368	22.0	4.7	1.413	0.589
40,0	6.3	5.237	0.465	40.0	6.3	1.220	0.781
62.0	7.9	4.037	0.600	60.0	7.9	1.072	0.931
80.0	8.9	3.844	0.604	82.0	8.9	0.966	1.035
100.0	10.0	3.376	0.651	100.0	10.0	0.895	1.106
132.0	11.5	2.644	0.740	120.0	11.5	0.839	1.164
180.0	13.4	2.227	0.781	180.0	13.4	0.699	1.304
240.0	15.5	1.830	0.821	240.0	15.5	0.608	1.395
300.0	17.3	1.566	0.847	300.0	17.3	0.552	1.451

Table A2.16 Continued.

Time (mins)	Time$^{\frac{1}{2}}$ ($min^{\frac{1}{2}}$)	Concentration $\times 10^{3}$ M	Uptake mol Kg^{-1}	Time (mins)	Time$^{\frac{1}{2}}$ ($min^{\frac{1}{2}}$)	Concentration $\times 10^{3}$ M	Uptake mol Kg^{-1}
Initial Concentration 2.979×10^{-3} M				Initial Concentration 3.974×10^{-3} M			
2.0	1.4	2.828	0.151	2.0	1.4	3.796	0.178
5.0	2.2	2.644	0.335	5.0	2.2	3.584	0.389
6.0	2.4	2.603	0.375	6.0	2.4	3.559	0.415
8.3	2.9	2.522	0.456	8.0	2.8	3.406	0.568
10.0	3.2	2.384	0.595	10.0	3.2	3.288	0.684
12.0	3.5	2.395	0.583	12.2	3.5	3.247	0.727
15.0	3.9	2.275	0.706	15.0	3.9	3.165	0.807
18.0	4.2	2.267	0.710	18.0	4.2	3.095	0.879
22.0	4.7	2.186	0.791	22.0	4.7	2.987	0.987
40.0	6.3	1.886	1.093	40.0	6.3	2.756	1.215
75.0	8.7	1.676	1.303	60.0	7.7	2.786	1.189
140.0	10.0	1.543	1.436	85.0	9.2	2.310	1.660
100.0	11.8	1.444	1.535	166.0	10.3	2.200	1.770
184.0	13.6	1.459	1.520	180.0	13.4	2.288	1.687
240.0	15.5	1.274	1.705	240.0	15.5	2.110	1.865
300.0	17.3	1.195	1.784	309.0	17.6	2.039	1.936

Table A2.16 Continued.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 4 969 x 10^{-3} M			
2.0	1.4	4.726	0.242
5.0	2.2	4.454	0.515
6.0	2.4	4.406	0.562
8.3	2.9	4.325	0.643
10.0	3.2	4.210	0.757
12.0	3.5	4.142	0.827
15.0	3.9	4.067	0.902
18.0	4.2	3.966	1.001
22.0	4.7	3.837	1.130
40.7	6.4	3.591	1.378
60.0	7.7	3.400	1.542
80.6	9.0	3.178	1.791
100.0	10.0	3.066	1.903
120.0	11.0	3.027	1.915
180.0	13.4	2.841	2.101
240.0	15.5	2.700	2.242
300.0	17.3	2.583	2.359

Table A2.17 The Rate of Uptake Data for 4-nitrophenol on to 2.0 gramme of Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30° at Various Initial Concentrations.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{4}$	Uptake $mol\ Kg^{-1} \times 10^{2}$	Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 9.990×10^{-4}				Initial Concentration 1.952×10^{-3} M			
1.0	1.0	9.406	2.92	2.0	1.4	1.745	0.103
4.0	2.0	8.287	8.49	5.0	2.2	1.538	0.206
9.0	3.0	6.673	16.54	6.0	2.4	1.493	0.229
13.0	3.6	5.834	20.72	8.0	2.8	1.395	0.278
16.0	4.0	5.318	23.29	10.0	3.2	1.281	0.334
20.0	4.5	4.792	25.91	12.0	3.5	1.197	0.376
25.0	5.0	4.210	28.82	15.0	3.9	1.131	0.409
36.0	6.0	3.234	33.68	18.0	4.2	1.045	0.452
60.0	7.8	2.207	38.40	22.0	4.7	0.941	0.504
129.0	11.4	1.164	43.60	40.0	6.3	0.754	0.597
180.0	13.4	0.915	44.90	60.0	7.7	0.577	0.692
240.0	15.5	0.778	45.60	80.0	8.9	0.421	0.762
300.0	17.3	0.676	46.10	120.0	10.9	0.322	0.819
2.0	1.4	9.024	4.83	180.0	13.3	0.231	0.864
6.0	2.4	7.461	12.12	240.0	15.4	0.191	0.884
22.0	4.7	4.576	26.55	300.0	17.7	0.165	0.897
18.0	4.2	5.023	24.29				

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Table A2.17 Continued.

Time (min)	Time$^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake mol Kg^{-1}	Time (min)	Time$^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake mol Kg^{-1}
Initial Concentration 2.964×10^{-3} M				Initial Concentration 3.961×10^{-3} M			
2.0	1.4	2.928	0.018	2.0	1.4	3.564	0.199
5.0	2.2	2.329	0.317	5.0	2.2	3.259	0.350
6.0	2.4	2.278	0.343	6.0	2.4	3.137	0.413
8.1	2.8	2.335	0.315	8.0	2.8	3.000	0.481
10.0	3.2	2.005	0.479	10.0	3.2	2.878	0.539
12.0	3.5	1.969	0.498	12.0	3.5	2.771	0.596
15.0	3.9	1.779	0.592	15.0	3.9	2.588	0.684
18.0	4.2	1.739	0.613	18.0	4.2	2.486	0.739
22.0	4.7	1.622	0.672	22.0	4.7	2.329	0.817
40.0	6.3	1.180	0.892	40.0	6.3	1.983	0.985
60.0	7.7	0.999	0.980	60.0	7.7	1.528	1.211
80.0	8.9	0.783	1.090	120.0	11.0	1.055	1.447
100.0	10.0	0.695	1.134	180.0	13.4	0.831	1.558
120.0	11.0	0.634	1.162	300.0	17.3	0.605	1.671
180.0	13.4	0.480	1.238	360.0	19.0	0.549	1.699
240.0	15.4	0.399	1.279				
300.0	17.3	0.356	1.300				

Table A2.17 Continued.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 4.915×10^{-3} M			
2.0	1.4	4.499	0.241
5.0	2.2	4.110	0.403
6.0	2.5	4.025	0.477
8.0	2.8	3.864	0.557
10.0	3.2	3.692	0.612
13.0	3.6	3.800	0.589
15.0	3.9	3.413	0.751
18.0	4.2	3.235	0.871
22.0	4.7	3.082	0.947
40.0	6.3	2.557	1.180
60.0	7.7	2.334	1.286
80.0	8.9	1.968	1.474
100.0	10.0	1.754	1.581
120.0	11.0	1.767	1.569
180.0	13.4	1.426	1.739
240.0	15.5	1.246	1.828
300.0	17.3	1.103	1.899

Table A2.18 The Rate of Uptake for 4-nitrophenol on to 0.5 gramme of Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30^{o}.

Time (min)	Time$^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration x 10^{3} M	Uptake mol Kg^{-1}
Initial Concentration 1.983 x 10^{-3} M.			
2.0	1.4	1.934	0.088
5.0	2.2	1.952	0.019
6.0	2.4	1.879	0.198
8.0	2.8	1.838	0.279
10.0	3.2	1.795	0.365
13.0	3.6	1.777	0.400
15.0	3.9	1.751	0.453
18.0	4.2	1.716	0.521
22.0	4.7	1.701	0.551
49.0	7.0	1.520	0.914
60.0	7.7	1.482	1.000
80.0	8.9	1.403	1.148
100.0	10.0	1.340	1.273
120.0	11.0	1.340	1.283
192.0	13.9	1.235	1.492
252.0	15.9	1.157	1.648
300.0	17.3	1.139	1.684

Table A2.19 The Rate of Uptake Data for 4-methoxybenzoic acid on to 1.0 gramme of Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30^{o}.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{4}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 1.003×10^{-3} M.			
2.0	1.4	9.420	0.061
5.0	2.2	9.339	0.068
6.0	2.4	8.627	0.140
8.0	2.8	8.303	0.172
10.0	3.2	7.785	0.224
12.0	3.5	7.785	0.224
15.0	3.9	7.348	0.268
18.0	4.2	7.251	0.277
22.0	4.7	6.862	0.316
60.0	7.7	4.066	0.497
76.0	8.7	4.050	0.598
120.0	11.0	3.548	0.648
180.0	13.4	2.836	0.720
240.0	15.5	2.460	0.758
300.0	17.3	2.033	0.800

Table A2.20 The Rate of Uptake Data for ethyl 4-aminobenzoate on to 1.0 gramme of Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30°.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake $mol\ Kg^{-1}$	Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{4}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 4.925×10^{-3} M				Initial Concentration 9.850×10^{-4} M.			
2.0	1.4	4.794	0.131	2.0	1.4	8.980	0.061
5.0	2.2	4.688	0.238	5.0	2.2	8.509	0.134
6.0	2.4	4.580	0.345	6.0	2.4	8.310	0.218
8.0	2.8	4.466	0.459	8.0	2.8	8.038	0.155
12.0	3.5	4.427	0.498	10.0	3.2	7.859	0.198
18.0	4.2	4.310	0.615	12.0	3.5	7.513	0.207
22.0	4.7	4.261	0.664	15.0	3.9	7.444	0.240
40.0	6.3	4.144	0.781	18.0	4.2	7.056	0.253
60.0	7.7	4.088	0.837	22.0	4.7	6.738	0.285
100.0	10.0	4.061	0.913	30.0	5.5	6.530	0.306
120.0	11.0	4.019	1.030	40.0	6.3	5.922	0.392
180.0	13.4	3.756	1.169	60.0	7.7	5.258	0.458
240.0	15.5	3.673	1.252	102.0	10.1	4.427	0.541
288.0	17.0	3.729	1.245	180.0	13.4	3.722	0.588
319.0	17.9	3.659	1.315	240.0	15.5	3.293	0.631
				300.0	17.3	2.892	0.671

A2.21

Table A2.21 The Rate of Uptake Data for 4-nitrophenol on to 1.0 gramme of Nylon 6 Coated Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30^{o}.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{4}$	Uptake $mol\ Kg^{-1}$	Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 1.004×10^{-3} M				Initial Concentration 1.988×10^{-3} M.			
6.0	2.5	9.456	0.038	6.0	2.5	1.881	0.107
13.0	3.6	9.151	0.069	12.0	3.5	1.833	0.155
22.0	4.7	8.644	0.120	20.0	4.5	1.751	0.231
26.0	5.1	8.427	0.141	26.0	4.9	1.729	0.260
30.0	5.5	8.263	0.158	30.0	5.5	1.642	0.344
36.0	6.0	8.109	0.173	40.0	6.3	1.622	0.367
48.0	6.9	7.626	0.222	48.0	6.9	1.602	0.387
60.0	7.7	7.088	0.296	60.0	7.7	1.525	0.464
96.0	9.8	6.381	0.346	120.0	11.0	1.228	0.755
134.0	11.6	5.835	0.401	150.0	12.2	1.146	0.837
150.0	12.2	5.267	0.478	210.0	14.5	0.976	1.004
180.0	13.4	5.098	0.475	264.0	16.2	0.923	1.059
217.0	14.7	4.614	0.523	270.0	16.4	0.938	1.040
240.0	15.5	4.220	0.583	300.0	17.3	0.877	1.104
270.0	16.4	4.170	0.568				
309.0	17.6	3.732	0.632				

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Table A2.21 Continued.

Time (min)	Time $^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration $\times 10^{3}$ M	Uptake mol Kg^{-1}	Time (min)	Time $^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration $\times 10^{3}$ M	Uptake mol Kg^{-1}
Initial Concentration 2.969 x 10^{-3} M				Initial Concentration 3.955 x 10^{-3} M			
6.0	2.4	2.796	0.173	6.0	2.4	3.808	0.147
12.0	5.5	2.725	0.244	12.0	3.5	3.661	0.294
20.0	4.5	2.699	0.270	20.0	4.5	3.503	0.413
25.0	5.0	2.573	0.395	24.0	4.9	3.513	0.443
30.0	5.5	2.491	0.477	30.0	5.5	3.401	0.515
31.0	5.6	2.547	0.420	36.0	6.0	3.406	0.550
36.0	6.0	2.445	0.523	48.0	6.9	3.315	0.641
46.0	6.8	2.384	0.584	60.0	7.7	3.417	0.809
60.0	7.7	2.283	0.685	90.0	9.5	2.801	1.116
120.0	11.0	2.074	0.891	120.0	11.0	2.888	1.025
150.0	12.2	1.968	0.997	160.0	12.6	2.750	1.163
214.0	14.6	1.820	1.147	210.0	14.5	2.573	1.340
240.0	15.5	1.759	1.205	240.0	15.5	2.593	1.320
270.0	16.4	1.729	1.238	270.0	16.4	2.415	1.502
300.0	17.3	1.637	1.327	300.0	17.3	2.476	1.438

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Table A 2.21 Continued.

Time (min)	$Time^{\frac{1}{2}}$ ($mins^{\frac{1}{2}}$)	Concentration $M \times 10^{3}$	Uptake $mol\ Kg^{-1}$
Initial Concentration 4.955×10^{-3} M.			
10.0	3.2	4.617	0.338
20.0	4.5	4.460	0.492
30.0	5.5	4.285	0.669
40.0	6.3	4.223	0.729
50.0	7.1	4.142	0.812
60.0	7.7	4.060	0.891
80.0	8.9	3.993	0.958
100.0	10.0	3.911	1.039
120.0	11.0	3.803	1.147
160.0	12.6	3.752	1.240
242.0	13.4	3.552	1.405
300.0	15.6	3.355	1.500
360.0	17.3	3.292	1.666

Table A2.22 The Rate of Uptake Data for 4-methoxybenzoic acid on to 1.0 gramme of Nylon 6 Coated Active Carbon from 1000ml of Solution at pH 2.32 (0.5M ionic strength) and 30°.

Time (min)	Time $^{\frac{1}{2}}$ (mins $^{\frac{1}{2}}$)	Concentration M x 10^{4}	Uptake mol Kg^{-1}
6.0	2.4	9.452	0.062
13.0	3.6	9.102	0.097
20.0	4.5	8.753	0.135
24.0	4.9	8.533	0.154
30.0	5.5	8.222	0.188
36.0	6.0	8.299	0.177
48.0	6.9	7.742	0.233
60.0	7.7	7.510	0.256
140.0	11.8	5.807	0.430
142.0	11.9	5.606	0.450
150.0	12.2	5.477	0.463
220.0	14.8	4.881	0.522
240.0	15.5	4.558	0.555
270.0	16.4	4.350	0.575
300.0	17.3	4.066	0.604

Initial Concentration 1 007 x 10^{-3} M

Table A 2.23 The Rate of Uptake Data for Ethyl 4-aminobenzoate on to 1.0 gramme of Nylon 6 Coated Active Carbon from 1000 ml of Solution at pH 2.32 (0.5M ionic strength) and 30°.

Time (min.)	Time$^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration M x 10^{3}	Uptake mol Kg^{-1}	Time (min.)	Time$^{\frac{1}{2}}$ (mins$^{\frac{1}{2}}$)	Concentration M x 10^{4}	Uptake mol Kg^{-1}
Initial Concentration 4.974 x 10^{-3} M				Initial Concentration 9.851 x 10^{-4}M.			
5.0	2.2	4.918	0.132	6.0	2.4	9.394	0.046
6.0	2.4	4.842	0.132	12.0	3.5	8.994	0.086
10.0	3.2	4.912	0.138	24.0	4.9	8.702	0.115
24.0	4.9	4.683	0.291	25.0	5.0	8.440	0.142
30.0	5.5	4.649	0.325	30.0	5.5	8.301	0.155
40.0	6.3	4.573	0.401	36.0	6.0	8.329	0.152
48.0	6.9	4.552	0.422	48.0	6.9	8.066	0.178
60.0	7.7	4.490	0.484	60.0	7.7	7.817	0.203
63.0	7.9	4.434	0.540	62.0	7.9	7.568	0.228
120.0	11.0	4.330	0.644	100.0	10.0	7.111	0.275
150.0	12.2	4.227	0.747	104.0	10.2	6.821	0.303
160.0	12.6	4.289	0.761	150.0	12.2	6.337	0.352
180.0	13.4	4.199	0.775	240.0	15.5	5.756	0.411
200.0	14.1	4.227	0.823	270.0	16.4	5.506	0.436
210.0	14.5	4.171	0.803	300.0	17.3	5.078	0.478
240.0	15.5	4.144	0.906				
285.0	16.9	4.123	0.851				
300.0	17.3	4.012	0.962				

Table A 2.24 Data for the Competitive Adsorption Kinetics of Ethyl 4-aminobenzoate on to 1 0 gramme of Active Carbon from 1000ml of Binary Mixed Solute Solution at pH 2.32 (0 5M ionic strength) and 30° in the Presence of 4-nitrophenol

Determination I : Initial Concentration : ethyl 4-aminobenzoate 4.948 x 10^{-3} M ; 4-nitrophenol 9.895 x 10^{-4}M

Time (min)	ethyl 4-aminobenzoate x 10^{3} M	4-nitrophenol x 10^{3} M	ethyl 4-aminobenzoate mol Kg^{-1}	4-nitrophenol mol Kg^{-1}
2.0	4.838	0.941	0.110	0.049
5.0	4.710	0.888	0.443	0.106
6.0	4.755	0.902	0.193	0.087
8.0	4.670	0.867	0.278	0.123
10.0	4.638	0.864	0.515	0.130
12.0	4.308	0.868	0.641	0.122
18.0	4.388	0.846	0.561	0.144
22.0	4.390	0.813	0.559	0.177
30.0	4.315	0.791	0.632	0.199
40.0	4.225	0.766	0.723	0.228
60.0	4.122	0.732	0.824	0.257
90.0	3.980	0.709	0.968	0.286
120.0	3.950	0.671	0.998	0.324
180.0	3.815	0.632	1.131	0.357
240.0	3.663	0.597	1.281	0.392
350.0	3.548	0.584	1.397	0.404

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Table A 2 24 Continued

Determination II : Initial Concentration : ethyl 4-aminobenzoate 9.950×10^{-4} M, 4-nitrophenol 4.975×10^{-3} M

Time (min)	ethyl 4-aminobenzoate $\times 10^{3}$M	4-nitrophenol $\times 10^{3}$ M	ethyl 4-aminobenzoate mol Kg^{-1}	4-nitrophenol mol Kg^{-1}
2.0	1.022	4.748	0.000	0.227
5.0	0.986	4.448	0.009	0.607
8.0	0.956	4.390	0.048	0.586
10.0	0.948	4.330	0.047	0.724
12.0	0.865	4.317	0.138	0.659
15.0	0.885	4.294	0.110	0.760
22.0	0.860	4.053	0.143	0.923
30.0	0.831	3.994	0.190	1.060
40.0	0.822	3.873	0.173	1.181
60.0	0.777	3.755	0.244	1.299
90.0	0.725	3.576	0.270	1.478
125.0	0.679	3.397	0.316	1.657
180.0	0.641	3.218	0.379	1.836
240.0	0.601	3.140	0.419	1.913
300.0	0.581	3.040	0.439	2.013

Table A 2.25 Data for the Competitive Adsorption Kinetics of 4-methoxybenzoic acid on to 1.0 gramme of Active Carbon from 1000 ml of Binary Mixed Solute Solution at pH 2.32 (0.5M ionic strength) and 30° in the Presence of Ethyl 4-aminobenzoate.

Initial Concentration 4-methoxybenzoic acid 1.005×10^{-3} M ethyl 4-aminobenzoate 4.935×10^{-3} M

Time (min)	Concentration		Uptake	
	4-methoxybenzoic acid $\times 10^{4}$ M	ethyl 4-aminobenzoate $\times 10^{3}$ M	4-methoxybenzoic acid mol Kg^{-1}	ethyl 4-aminobenzoate mol Kg^{-1}
2.0	0.929	4.786	0.051	0.149
5.0	0.902	4.624	0.103	0.230
6.0	0.881	4.636	0.099	0.299
8.0	0.881	4.601	0.099	0.334
10.0	0.863	4.486	0.142	0.368
12.0	0.860	4.521	0.120	0.414
15.0	0.833	4.487	0.172	0.367
18.0	0.795	4.418	0.185	0.517
22.0	0.800	4.395	0.181	0.540
30.0	0.789	4.279	0.217	0.620
40.0	0.765	4.233	0.239	0.620
60.0	0.753	4.164	0.253	0.735
93.0	0.681	4.003	0.323	0.850
120.0	0.657	3.923	0.349	0.976
150.0	0.640	3.842	0.365	1.010
180.0	0.615	3.796	0.390	1.102
240.0	0.608	3.704	0.397	1.194

Table A 2.26 Data for the Competitive Adsorption Kinetics of 4-methoxybenzoic acid on to 1.0 gramme of Active Carbon from 1000ml of Binary Mixed Solution at pH 2.32 (0.5M ionic strength) and 30^{o} in the Presence of 4-nitrophenol.

Initial Concentration 4-methoxybenzoic acid 1.001×10^{-3} M : 4-nitrophenol 5.001×10^{-3} M

Time (min)	Concentration 4-methoxybenzoic acid x 10 M	4-nitrophenol x 10^{3} M	Uptake 4-methoxybenzoate acid mol Kg^{-1}	4-nitrophenol mol Kg^{-1}
2.0	0.967	4.683	0.033	0.315
5.0	0.906	4.481	0.093	0.521
6.0	0.915	4.528	0.085	0.471
8.0	0.876	4.366	0.124	0.633
10.0	0.863	4.345	0.137	0.659
12.0	0.837	4.277	0.162	0.722
15.0	0.811	4.210	0.188	0.793
18.0	0.794	4.135	0.205	0.863
22.0	0.768	4.074	0.231	0.924
30.0	0.708	3.908	0.291	1.090
40.0	0.695	3.871	0.304	1.133
60.0	0.627	3.686	0.372	1.312
98.0	0.583	3.538	0.416	1.468
120.0	0.548	3.389	0.451	1.617
180.0	0.506	3.311	0.494	1.687
308.0	0.437	2.023	0.562	2.023

Table A 2.27 Data for the Competitive Adsorption Kinetics of Ethyl 4-aminobenzoate on to 1.0 gramme of Nylon 6 Coated Active Carbon from 1000ml of a Binary Mixed Solution at pH 2.32 (0.5M ionic strength) and 30° in the Presence of 4-nitrophenol.

Determination I Initial Concentration ethyl 4-aminobenzoate 5.153×10^{-3} M 4-nitrophenol 9.943×10^{-4} M

Time (min)	Concentration		Uptake	
	ethyl 4-aminobenzoate $\times 10^{3}$ M	4-nitrophenol $\times 10^{3}$ M	ethyl 4-aminobenzoate mol Kg^{-1}	4-nitrophenol mol Kg^{-1}
8.0	5.025	0.881	0.128	0.113
20.0	4.868	0.887	0.252	0.067
30.0	4.843	0.867	0.278	0.088
26.0	4.903	0.854	0.249	0.140
40.0	4.785	0.849	0.335	0.105
48.0	4.825	0.843	0.329	0.151
60.0	4.750	0.819	0.371	0.135
90.0	4.576	0.788	0.545	0.166
150.0	4.548	0.748	0.373	0.207
150.0	4.480	0.744	0.640	0.211
210.0	4.345	0.707	0.775	0.247
240.0	4.316	0.703	0.806	0.251
270.0	4.340	0.682	0.780	0.272
300.0	4.305	0.685	0.817	0.269

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Table A 2.27 Continued.

Determination II Initial Concentration ethyl 4-aminobenzoate 9.950×10^{-4} M : 4-nitrophenol 4.975×10^{-3} M.

Time (min)	Concentration		Uptake	
	ethyl 4-aminobenzoate $\times 10^{3}$ M	4-nitrophenol $\times 10^{3}$ M	ethyl 4-aminobenzoate mol Kg^{-1}	4-nitrophenol mol Kg^{-1}
6.0	0.994	4.793	0.027	0.182
12.0	1.034	4.647	0.000	0.327
20.0	0.987	4.570	0.034	0.403
24.0	0.970	4.551	0.051	0.423
30.0	0.915	4.414	0.088	0.637
36.0	0.937	4.312	0.084	0.562
48.0	0.918	4.271	0.103	0.702
60.0	0.911	4.212	0.110	0.838
91.0	0.865	4.032	0.129	0.938
150.0	0.800	3.853	0.194	1.194
210.0	0.807	3.590	0.187	1.377
240.0	0.808	3.598	0.191	1.448
300.0	0.809	3.589	0.193	1.457

Table A 2.28 Data for the Competitive Adsorption Kinetics of 4-methoxybenzoic acid on to 1.0 gramme of Nylon 6 Coated Active Carbon from 1000 ml of Binary Mixed Solute Solution at pH 2.32 (ionic strength 0.5M) at 30^{o} in the Presence of Ethyl 4-aminobenzoate.

Initial Concentration	4-methoxybenzoic acid 1.005×10^{-3} M	Ethyl 4-amino-benzoate $4\ 935 \times 10^{-3}$ M		
	Concentration		Uptake	
Time (min)	4-methoxybenzoic acid $\times 10^{4}$ M	ethyl 4-aminobenzoate $\times 10^{3}$ M	4-methoxybenzoic acid mol Kg^{-1}	4-aminobenzoate mol Kg^{-1}
6.0	9.680	4.762	0.034	0.184
12.0	9.670	4.739	0.033	0.207
24.0	9.155	4.612	0.085	0.334
30.0	9.315	4.624	0.105	0.340
40.0	8.945	4.532	0.106	0.413
48.0	8.690	4.509	0.131	0.436
60.0	8.510	4.452	0.149	0.493
90.0	8.450	4.371	0.191	0.612
100.0	8.440	4.359	0.157	0.589
150.0	8.130	4.290	0.188	0.658
200.0	7.800	4.233	0.256	0.749
240.0	7.565	4.129	0.245	0.820
270.0	7.450	4.129	0.291	0.853
300.0	7.375	4.129	0.264	0.820

Table A 2.29 Data for the Competitive Adsorption Kinetics of 4-methoxybenzoic acid on to 1.0 gramme of Nylon 6 Coated Active Carbon from 1000 ml of Binary Mixed Solution at pH 2.32 (ionic strength 0.5M) and 30^{o} in the Presence of 4-nitrophenol.

Initial Concentration	4-methoxybenzoic acid 1.001×10^{-3} M		4-nitrophenol 5.001×10^{-3} M.	
	Concentration		Uptake	
Time (min)	4-methoxybenzoic acid $\times 10^{4}$ M	4-nitrophenol $\times 10^{3}$ M	4-methoxybenzoic acid mol Kg^{-1}	4-nitrophenol mol Kg^{-1}
6.0	0.971	4.664	0.029	0.337
13.0	0.945	4.596	0.055	0.405
20.0	0.902	4.440	0.098	0.561
24.0	0.911	4.474	0.090	0.527
30.0	0.872	4.338	0.128	0.663
36.0	0.876	4.345	0.124	0.657
48.0	0.850	4.264	0.150	0.738
60.0	0.807	4.142	0.192	0.855
66.0	0.816	4.169	0.184	0.833
95.0	0.768	3.952	0.232	1.049
100.0	0.747	3.945	0.252	1.051
150.0	0.695	3.728	0.305	1.273
215.0	0.639	3.572	0.362	1.429
240.0	0.630	3.593	0.369	1.402
276.0	0.609	3.477	0.392	1.524
300.0	0.596	3.518	0.403	1.477

APPENDIX 3

CALCULATION

of the

DIFFUSION COEFFICIENT for SOLUTE MASS TRANSFER

in

ACTIVE CARBON

THE CHARACTERISATION of DIFFUSION with NON-LINEAR ADSORPTION.

The diffusion of solute molecules within carbon granules gives rise to the long equilibration times characteristic of such sorbent materials. The present section represents an approach to the partial characterisation of intraparticle mass transfer by the separation and evaluation of the diffusive component of this process. Measurements of the rate of sorption, together with separate measurement of the sorption isotherm are used to obtain the average diffusion coefficient from a numerical integration of the conservation of diffusing mass equation. This technique permits reduction of experimental kinetic profile data to a common parameter to facilitate system-to-system comparisons.

A.3.1 The Conservation of Diffusing Mass Equation.

During the process of adsorption, mass is conserved but distributed within the sorbent granule and the bulk solution. The conservation of diffusing mass equation (Equation A.3.1) represents the mass transfer within the granule. In highly active carbons, solute molecules may be either adsorbed or free to diffuse, both processes being of equal importance.

$$\frac{dC_c}{dt} = \frac{\bar{D}d^2C_c}{dx} - \frac{dN_c}{dt} \quad \ldots\ldots\ldots\ldots \text{(A.3.1)}$$

where C_c = the concentration of solute in the carbon free to diffuse

t = time

x = distance with respect to the direction of mass transfer

N_c = the mass of solute adsorbed and not free to diffuse

$\bar{D}$ = the diffusion coefficient

Equation A.3.1 states that the rate of intraparticle mass transfer is given by $dC_c/dt + dN_c/dt$ which ultimately affects the rate of removal of solute from solution. The solution of equation A.3.1 is virtually impossible by standard calculus due to the complexity introduced by the non-linear isotherm. The numerical integration of equation A.3.1 is relatively more simple and will be presented here.

A.3.2 Reduced Variables.

The relationship given in equation A.3.1 describes the general diffusion situation for one dimension only, however, if the active carbon sorbent is taken to be spherical, equation A.3.1 must be modified to account for three dimensional mass flow. In spherical co-ordinates, mass diffuses and is deposited along the sphere radius which is referred to as radial flow. The equation corresponding to radial flow which is equivalent to equation A.3.1, is given in equation A.3.2.

$$\frac{dC_c}{dt} = \frac{\bar{D}}{r^2} \frac{d}{dr}\left(r^2 \cdot \frac{dC_c}{dr} \right) - \frac{dN_c}{dt} \quad \text{.....(A3.2)}$$

where r = the radial distance moved by the solute after time t.

Equation A3.2 can be solved provided that certain boundary conditions are defined to account for mass transfer between the solution phase and the carbon phase. The boundary condition appropriate to sorption from a limited volume is the conservation of diffusing mass equation (equation A.3.3).

$$VC_o = VC'_c \times \int_{r=o}^{r=a} (C_c + N_c)\ 4\pi r^2.dr \quad \text{.....(A.3.3)}$$

where V = solution volume.

C_o = initial concentration of solute.

C'_c = the concentration at the boundary of the granule(s)

a = the radius of the carbon sorbent.

x = the number of carbon granules present.

The term VC_o defines the total mass in the solute which after commencement of the determination exists either in solution, VC_B, or in the sorbent, given by the integral term in equation (A.3.3). The rate at which the solution is depleted of solute will therefore depend upon the numerical value of the integral term which in turn is obtained by solution of equation (A.3.2).

The solution of equation A.3.2 involving the determination of D, by the Crank-Nicholson method of numerical approximation is more conveniently achieved using dimensionless or reduced variables. The variables used in equations A.3.2 and A.3.3 are reduced as follows

$$c = \frac{C_c}{C_o}, \quad n = \frac{N_c}{C_o}, \quad \rho = \frac{r}{a} \quad \& \quad \tau = \frac{\bar{D}t}{a^2}$$

Using these reduced variables, equations A.3.2 and A.3.3 may be re-written

$$\frac{dc}{d\tau} = \frac{1_2}{\rho} \cdot \frac{d}{d\rho}\left(\rho^2 \cdot \frac{dc}{d\rho}\right) - \frac{dn}{d\tau} \quad \text{.....(A.3.4)}$$

fore be superimposed upon the experimental curve by adjusting the numerical value of $\bar{D}$. The value of $\bar{D}$ that achieves the highest degree of coincidence is the solution to equation A.3.2 for the boundary condition given in equation A.3.5 and the initial condition :

$c = 0$ at $\tau = 0$ for $0 \leq \rho \leq 1$.

The solution of equation A.3.2 using the Crank-Nicholson method is laborious and, as such, is more easily achieved by computer. A modified version of a programme developed by Weber and Rumer (Section 1.6.2.) is given in appendix 4.

This program is used for all determinations of $\bar{D}$.

A.3.6 THE CALCULATION OF $\bar{D}$ BY CURVE MATCHING OF SIMULATED AND EXPERIMENTAL RESULTS.

A.3.6.1 The Diffusion of 4-nitrophenol in Active Carbon.

The sorption rate profiles of 4-nitrophenol by active carbon were used to examine the validity of the pore diffusion with adsorption model and the subsequent method of calculating $\bar{D}$. The calculation procedure should give rise to a constant value of $\bar{D}$ for differing conditions of initial concentration and granule weight.

A.3.6.2 Implementation of the Calculation Procedure.

The computer programme was initially run to generate the theoretical sorption kinetic profile using 8 to 20 concentric shells to obtain optimum accuracy of plotting over the full range of residual concentration. The experimental and simulated curves for the sorption of 4-nitrophenol on to 2 gramme of active carbon from 1000 ml of a 10^{-3} M solution at 30^{o} and pH 2.32 (0.5M ionic strength) are given in figures 4.5 and 4.4 respectively.

distance can be represented graphically, as shown in figure A.3.1.

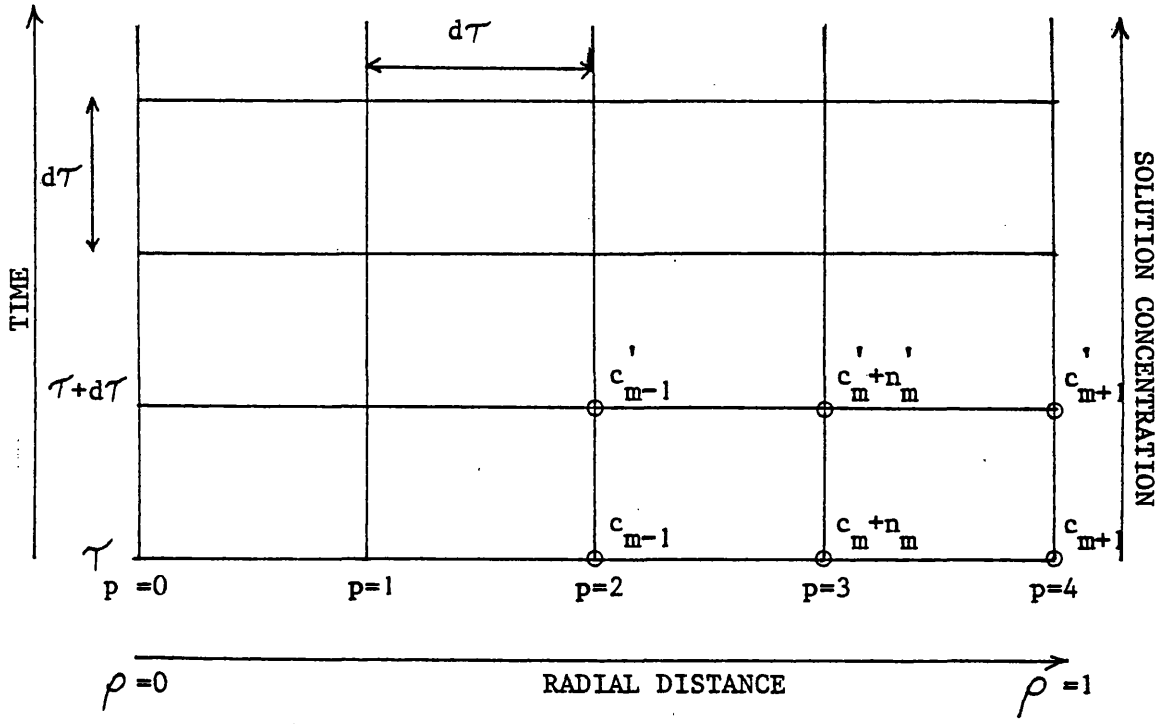


Figure A.3.1 Schematic Representation of the Elements of the Diffusion Space and Time for a Homogeneous Sphere Representing an Active Carbon Granule.

Figure A.3.1 shows a sphere radius which has been subdivided into 4 shells (p = 4) of equal distance, $d\rho$, such that $d\rho = 0.25p$. The solute concentration at the surface and the interface between shells 3 and 4, and 2 and 3 are designated c_{m+1}, c_m and c_{m-1}, respectively. The concentration of solute at these points at the next increment in time, $\tau + d\tau$, are designated c'_{m+1}, c'_m, c'_{m-1}, respectively. The amount of solute immobilised at the interface between spheres 3 and 4 at time $= \tau$ and time $= \tau + d\tau$ are designated n_m and n'_m respectively.

$$\frac{3V}{4\pi a^3} = \frac{3VC'}{4\pi a^3} + 3x \int_{p=o}^{p=1} (c + n)\rho^2 .d\rho \ , \ .....(A.3.5)$$

A.3.3. Characterisation of Solute Flow in the Sorbent.

The initial mass of solute in the system at the commencement of the experiment and that which remains in solution after a certain elapsed time can be measured directly. The amount of solute present in the carbon granule and its distribution with respect to radial distance cannot be directly measured. As the rate controlling process is intrasorbent mass transfer it is necessary to simulate mass transfer within the sorbent, numerically, according to the characteristics of equation A.3.4 for the boundary condition given in equation A.3.5. The result of this procedure will be a simulated plot of c' versus τ .

If the model used to develop equation A.3.5 is an accurate representation of the actual process, the simulated curve of c' versus τ should have a similar functional form to the experimental residual concentration versus time curve $\bar{D}$ can be obtained by curve matching as described in section 1.6.2. .

A.3.4 The Use of Finite Difference Ratios to Obtain the Simulated Curve.

The differential terms in equation A.3.5 can be replaced by finite difference ratios (Crank 1956). The radius of the "spherical" sorbent is subdivided into p equal intervals of length $d\rho$ which effectively divides the resulting spherical solid of revolution into p concentric shells. The purpose of this procedure is to enable the concentration of solute at each shell-shell interface to be calculated with respect to time. The subdivision of time and

The letter p is used to indicate the absolute position of the interface with respect to the radius, and m is used to denote relative position, therefore with reference to the interface between shells three and four, m = (p-1)=3. The solution of equation A.3.4 is obtained by subdividing the time and radial dimensions into small increments such that the concentration change with respect to time and radial distance is essentially linear. If this approximation is made, the differentials in equation A.3.4 can be replaced by finite difference ratios as shown below

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\frac{\rho^2 . dc}{d\rho}\right) = \frac{1}{2m(d\rho^2)}\left\{\begin{array}{l}(m+1)(c_{m+1}+c'_{m+1}) - 2m\,(c_m + c'_m) \\ \quad + (m-1)(c_{m-1}+ c'_{m-1})\end{array}\right\} \quad ...(A.3.6)$$

$$\frac{dc}{d\tau} = \frac{c'_m - c_m}{d\tau} \quad ...(A.3.7)$$

$$\frac{dn}{d\tau} = \frac{n'_m - n_m}{d\tau} \quad ....(A.3.8)$$

Substitutions of the relationships in equations A.3.6, A.3.7 and A.3.8 into equation A.3.4 gives equation A.3.9

$$n'_m = n_m + \frac{d\tau}{2m(d\rho)^2}\left\{\begin{array}{l}(m+1)(c_{m+1} + c'_{m+1}) - 2m\,(c_m + c'_m) \\ \quad + (m-1)(c_{m-1} + c'_{m-1})\end{array}\right\} - (c'_m - c_m) \quad ... \quad (A.3.9)$$

With reference to figure A.3.1 equation A.3.9 is used to calculate n'_m at time $\tau + d\tau$, using the concentrations at the points in time indicated by the closed circles. Calculation of the distribution of solute within the granule with respect to time proceeds as follows.

1) The initial condition for the solution of the diffusion equation is :

$c = 0$ at $\tau = 0$ for $0 \leq \rho \leq 1$.

This means that the sorbent is initially free of solute which is present only in the supernatant solution. Consequently c, at p = 4. is equal to 1 , and at all other values of p it equals zero.

2) The value of n'_m at time = 0 + d where m=p-1 is obtained using equation A.3.9. At time = 0, c_{m+1} (c_4) equals 1 and c_m and c_{m-1} both equal zero. It is convenient to make the c' values equal the c values initially as the likely difference between them is small.

3) Values of n corresponding to values of c are obtained using the Langmuir equation in dimensionless form, replacing the normal variables with reduced variables (equation A.3.10).

$$n = \frac{\alpha\beta c}{1 + \beta c} \qquad \text{.....(A.3.10).}$$

where $\alpha = \frac{N_{cmax}}{c_0}$

$\beta = \frac{b}{c_0}$

4) Having calculated n'_m at m = p-1, n'_m at m = p-2 is obtained using equation A.3.9. All values of n' are calculated for the radius moving an interface towards the core of the sphere each time.

5) As m-1 where m = p-p i.e. the centre of the sphere where p=0, an approximate finite difference approximation to equation A.3.9 is used (equation A.3.11).

$$n'_o = n_o + \frac{3\,d\tau}{(d\rho^2)}\left\{(c'_1 + c_1) - (c'_o + c_o)\right\} - (c'_o - c_o) \quad \ldots \text{(A.3.11)}.$$

The procedure to this point is summarised in figure A.3.2 Sections 1 to 4.

6) When the whole time from m = p-1 to m=o has been evaluated $\int_o^1 (c + n)\rho^2 \cdot d\rho$ is readily calculated by using one of the well known formulae for numerical integration. For example, Simpson's one-third rule gives

$$\int_o^1 (c + n)\rho^2 \cdot d\rho = \frac{1}{3}(d\rho)^3\left\{p\,(c'_p + n'_p) + 4(p-1)(c'_{p-1} + n'(p-1)) \ldots\ldots + 4\,(c'_1 + u'_1)\right\} \ldots \text{(A.3.12)}$$

7) The calculated value of $\int_o^1 (c + n)\rho^2 \cdot d\rho$ is then substituted in to the boundary condition in equation A.3.5 to calculate c', this is c_4 at $\rho = 1$.

8) The values of c' calculated by this procedure are then used as new estimates and stages 1 - 7 are repeated until no difference is apparent between the estimated and calculated values.

9) The procedure is then restarted using the c and n values at time = 0 + 2dτ to calculate c and n values at time = 0 + dτ and so on.

The procedure to this point is summarised in figure A.3.2 Sections 5 and 6.

A.3.5 Curve Matching Procedures.

The calculation procedure, outlined in the preceding section, evaluates the boundary concentration, or the solution concentration as a function of τ . If the reduced variables are considered, it is apparent that c is the fraction of the initial concentration of solute at zero time and $\tau = \bar{D}t/a^2$. The simulated curve can there-

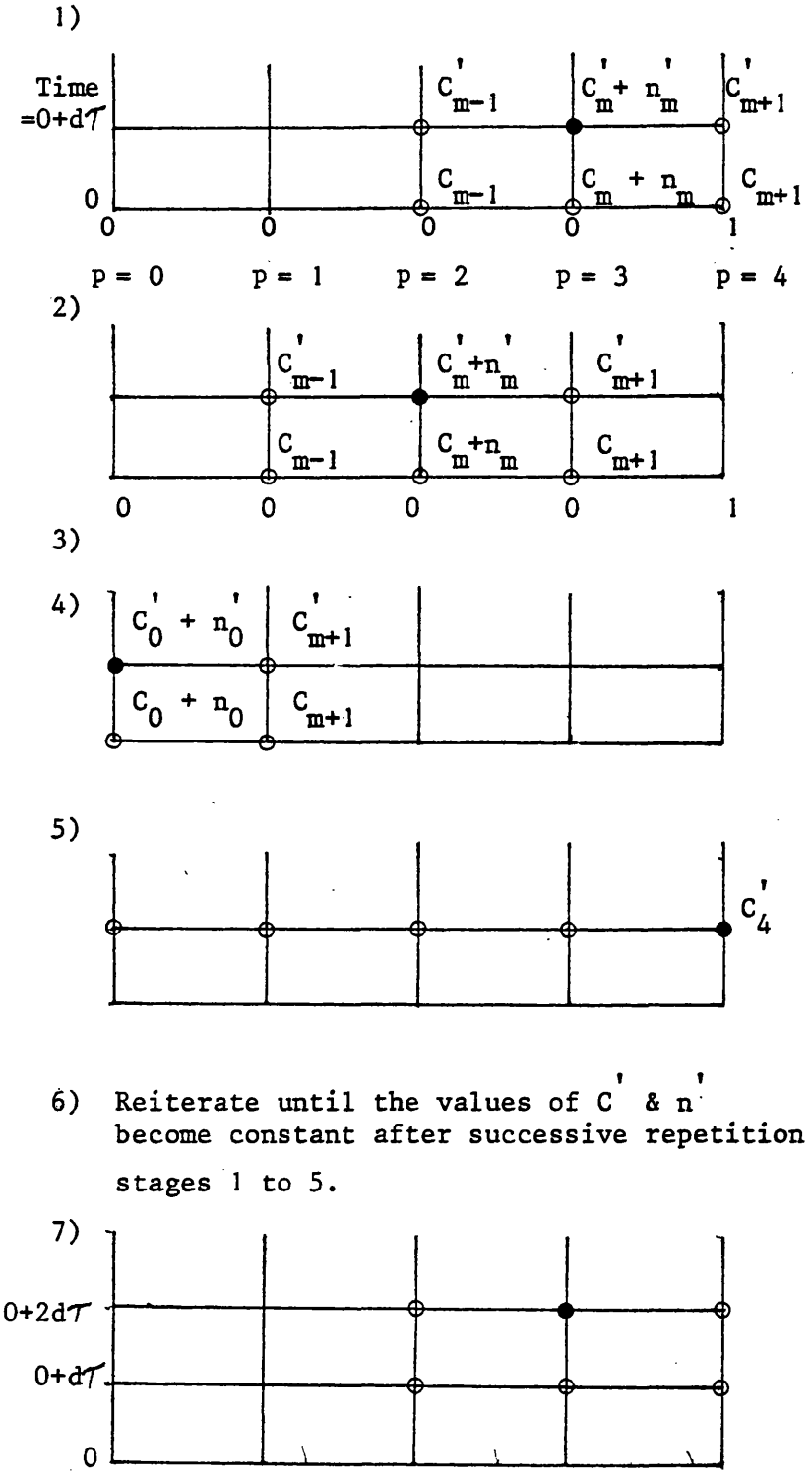
The similarity in the functional form of the simulated and experimental profile suggest that the model is a reasonably good representation of the sorption rate determining diffusion process. Fifteen values of percentage residual concentration were selected for the matching procedure which is summarised in table A3.1. The average diffusion coefficients obtained by this method are discussed in Section

Table A3.1 Calculation Table for the Calculation of $\bar{D}$ by Matching Experimental and Simulated Curves of the Sorption Kinetic Profile.

Percentage Residual Concentration	time (mins) from Fig.4.5	from Fig.4.4	Average Diffusion Coefficient $m^2\ sec^{-1}$
100	0.0	0.00	-
95	1.0	0.00	-
90	2.0	0.01	1.33×10^{-10}
85	3.0	0.05	4.45×10^{-10}
80	5.0	0.05	2.67×10^{-10}
75	6.0	0.10	4.45×10^{-10}
70	8.0	0.20	6.67×10^{-10}
65	10.0	0.35	9.33×10^{-10}
60	13.0	0.55	11.28×10^{-10}
55	16.0	0.85	14.17×10^{-10}
50	19.0	1.20	16.84×10^{-10}
45	23.0	1.75	20.29×10^{-10}
40	28.0	2.40	22.86×10^{-10}
35	34.0	3.30	25.89×10^{-10}
30	42.0	5.00	31.75×10^{-10}
25	53.0	7.70	38.75×10^{-10}
20	70.0	13.90	52.96×10^{-10}

mean $\bar{D} = 1.76 \times 10^{-9}$

standard deviation = 1.43×10^{-9}



m=3; Obtain n'_m & C'_m Using Eqns A3.9 & A3.10

m=2; Obtain n'_m & C'_m as above

m=1

m=0; Obtain n'_0 & C'_0 using Eqns A3.10 & A3.11

m=4; Obtain C'_4 the per cent residual concentration at time = $d\tau$ using eqns A3.12 & A3.15

6) Reiterate until the values of C' & n' become constant after successive repetition of stages 1 to 5.

Restart stage 1 for time=0+2dT

Figure A3.2: Schematic Representation of the Calculation of Mass Distribution in the Carbon Sorbents.

APPENDIX 4

COMPUTER PROGRAMS

```
implicit real*8(a-h,o-z)
dimension c(200),s(200),cnew(200),snew(200),cc(200)
dimension ctemp(200),stemp(200)
integer p,em
external condition_ (descriptors),nothing
 call condition_ ("underflow",nothing)
read(45,999)p,delt,tend,a,b,vol,radius,err,numb,icheck,cz,dens
write(6,3333)a,b,vol,radius
delr=1./p
ip=p+1
read(45,999)t
read(45,999)(c(i),i=1,ip)
do 10 i=1,ip
 cnew(i)=c(i)
s(i)=a*b*c(i)/(1.+b*dabs(c(i)))
snew(i)=s(i)
10 continue
  counter=0.0
15 m=ip-1
index=0
20 em=m-1
 coef=delt/(2.*em*delr*delr)
term=(em-1.)*(c(m-1)+cnew(m-1))
terms=(em+1.)*(c(m+1)+cnew(m+1))-2.*em*(c(m)+cnew(m))+term
if(snew(m)-cnew(m))28,28,25
25 ss=s(m)+coef*terms-(cnew(m)-c(m))
 cc(m)=dabs(ss/(a*b-ss*b))
if(dabs(ss-snew(m))-err*snew(m))29,29,30
28 cc(m)=c(m)+coef*terms-(snew(m)-s(m))
29 if(dabs(cc(m)-cnew(m))-err)40,40,30
30 index=1
40 cnew(m)=cc(m)
snew(m)=a*b*cnew(m)/(1.+b*dabs(cnew(m)))
if(m-2)1000,51,50
50 m=m-1
go to 20
51 if(snew(1)-cnew(1))60,60,55
55 ss=s(1)+(3.*delt/(delr*delr))*(cnew(2)+c(2))-(cnew(1)-c(1))
 cc(1)=dabs(ss/(a*b-ss*b))
if(dabs(ss-snew(1))-err*snew(1))61,61,70
60 cc(1)=c(1)+(3.*delt/(delr*delr))*(cnew(2)+c(2))-(snew(1)-s(1))
61 if(dabs(cc(1)-cnew(1))-err)80,80,70
70 index=1
80 cnew(1)=cc(1)
snew(1)=a*b*cnew(1)/(1.+b*dabs(cnew(1)))
sum1=0
sum2=0
ii=ip-1
90 ei=ii-1
```

Program A4.1: To Calculate the Diffusio
Coefficient of Active Carbon Using the
Method of Finite Differences and the
Conservation of Diffusing Mass Equation

```
sum1=sum1+ei*ei*(cnew(ii)+snew(ii))
if(ii-1)1000,120,100
100 ii=ii-1
ei=ii-1
sum2=sum2+ei*ei*(cnew(ii)+snew(ii))
if(ii-1)1000,120,110
110 ii=ii-1
go to 90
120 prod1=4.*sum1
prod2=2.*sum2
 coe=(delr*delr*delr)/3
gral=coe*(p*p*(cnew(ip)+snew(ip))+prod1+prod2)
 cc(ip)=1.-gral*4.*numb*3.14159*(radius**3)/vol
ss=a*b*cc(ip)/(1.+b*dabs(cc(ip)))
 if(dabs(cc(ip)-cnew(ip))-err)123,123,125
123 if(dabs(ss-snew(ip))-err*snew(ip))130,130,125
125 index=1.
130 cnew(ip)=cc(ip)
ut=cz*(1.0-cnew(ip))*vol/(numb*dens)
tpt5=dsort(t)
snew(ip)=ss
if(index)1000,140,15
140 t=t+delt
if(t-tend)160,1000,1000
160 do 170 i=1,ip
 ctemp(i)=c(i)
 stemp(i)=s(i)
 c(i)=cnew(i)
 s(i)=snew(i)
 cnew(i)=cnew(i)+(cnew(i)-ctemp(i))
 snew(i)=snew(i)+(snew(i)-stemp(i))
 counter=counter+1
if(1-counter)640,650,650
650 write(6,998)t,tpt5,cnew(ip),ut
640 continue
if(icheck-counter)1000,600,170
600 continue
 counter=0.0
170 continue
go to 15
1000 continue
stop
999 format(v)
998 format(d12.6,4x,d12.6,4x,d12.6,4x,d12.6)
997 format(12f10.4)
3333 format(4f10.2)
9876 format(7f10.8)
end
```

```
implicit real*8(a-h,o-z)
real heck
 common phi(2,110),der(2,110),con(2,110),p(2,3),vint(2,3),cia(2),xk(2),cor
dimension dat(5),xnabs(2),zc(2),ze(2),ssq(3),dev(3),xres(8)
read(56,1001)nn
1001 format(v)
do 3 j=1,3
3 ssq(j)=0.0
  call isetup
do 50 k=1.nn
read(56,1002)dat(2),dat(4),dat(3),dat(5),dat(1)
1002 format(v)
xnabs(1)=50*(dat(2)-dat(3))/dat(1)
xnabs(2)=50*(dat(4)-dat(5))/dat(1)
 cia(1)=dat(3)
 cia(2)=dat(5)
 call cansur(psin,ierr)
if (ierr.eq.1) stop
xtot=xnabs(1)+xnabs(2)
do 5 j=1,2
zc(j)=cia(j)/vint(j,1)
5 ze(j)=xnabs(j)/xtot
xtcal=0.0
do 10 j=1,2
xn=vint(j,1)*dinta(j,vint(j,1))
10 xtcal = xtcal + zc(j)/xn
xtcal = 1./xtcal
dev(1)=(xtcal-xtot)*100./xtot
dev(2)=(zc(1)-ze(1))*100.
dev(3)=(zc(2)-ze(2))*100
do 20 j=1,3
20 ssq(j)=ssq(j)+abs(dev(j))
xres(1)=cia(1)
xres(2)=cia(2)
xres(3)=xtot*ze(1)
xres(4)=xtcal*zc(1)
xres(5)=xtot*ze(2)
xres(6)=xtcal*zc(2)
xres(7)=xtot
xres(8)=xtcal
write(67,775)(xres(i),i=1,8),ze(1),zc(1),ze(2),zc(2),(dev(i),i=1,3)
775 format(!5(f10.6,1x))
50 continue
do 55 j=1,3
heck=float(nn)
mark=dble(heck)
55 ssq(j) = ssq(j)/mark
write(67,2003)(ssq(i),i=1,3)
2003 format(70x,3(2x,f8.3))
```

Program A4.2: To Calculate Multisolute Equili
from Single Solute Sorption Equilibrium Data.

```
      stop
      end
      subroutine canswr(psin,ierr)
      implicit real*8(a-h,o-z)
       common phi(2,110),der(2,110),con(2,110),p(2,3),vint(2,3),cia(2),xk(2),co
      dimension cxerr(2),cphi(2),ich(2)
      imax=50
       cxerr(1)=-100000.
       cxerr(2)=100000.
       cphi(1)=.0001
       cphi(2)=100000.
      ich(1)=-1
      ich(2)=-1
      ertol=.001
      icount=0
      plim=phi(1,2)
      if(phi(2,2).lt.plim) plim = phi(2,2)
       call datre(psin,ierr,0)
      psin=psin
      if(ierr.eq.1) go to 50
      3 icount = icount+1
      if(icount.gt.imax) go to 60
       call datre(psin,ierr,1)
      if(ierr.eq.0) go to 4
      ierr=0
      write(67,2001)
      4 derr=0.0
      xerr=1.0
      do 5 j=1,2
      xerr = xerr-cia(j)/vint(j,1)
      5 derr=derr + cia(j)*vint(j,2)/(vint(j,1)*vint(j,1))
      if(dabs(xerr).lt.ertol) go to 10
      if(xerr.lt.0.0.and.xerr.gt.cxerr(1)) go to 80
      if(xerr.gt.0.0.and.xerr.lt.cxerr(2)) go to 90
      go to 85
      80   cxerr(1) = xerr
       cphi(1)=psin
      ich(1)=1
      go to 85
      90 cxerr(2)=xerr
       cphi(2)=psin
      ich(2)=1
      85 if(ich(1).gt.0.and.ich(2).gt.0) go to 8
      psin=psin-xerr/derr
      if(icount.gt.20) psin=(cphi(1)+cphi(2))/2.
      if(psin.lt.plim)psin=plim
      go to 3
      8 psin=psin-xerr*(cphi(2)-cphi(1))/(cxerr(2)-cxerr(1))
      if (icount.gt.20) psin=(cphi(1)+cphi(2))/2.
```

```
      if(psin.lt.plim) psin=plim
      go to 3
   10 ierr=0
      go to 70
   50 write(67,2001)
 2001 format(10x,28hparameter table is too small )
      go to 65
   60 write(67,2002)
 2002 format(10x,36hconvergence count is greater than 50)
   65 ierr=1
   70 continue
      return
      end
      subroutine isetup
      implicit real*8(a-h,o-z)
       common phi(2,110),der(2,110),con(2,110),p(2,3),vint(2,3),cia(2),xk(2),cor
     dimension igap(9),xgap(9),ityp(9),cons(6)
     data(igap(i),i=1,9)/1,1,5,20,15,10,20,20,17/
     data(xgap(i),i=1,9)/.000004,.00001,.00005,.0005,.003,.01,.05,.15,.3/
     data(ityp(i),i=1,9)/5,5,1,1,1,1,1,1,1/
     data(cons(i),i=1,6)/19.0,75.0,50.0,50.0,75.0,19.0/
     do 5 j=1,2
    5 read(56,1001)(p(j,i),i=1,3)
 1001 format(v)
     do 7 j=1,2
    7 write(67,1001)(p(j,i),i=1,3)
     do 30 k=1,2
     idt=1
     phi(k,idt) =0.0
     if(k.eq.2) go to 8
     der(k,idt)=p(k,1)*p(k,2)
     go to 9
    8 der(k,idt)=p(k,1)*p(k,2)
    9 con(k,idt)=0.0
     do 25 j=1,9
     ig=igap(j)
     do 25 l=1,ig
     idt=idt+1
      con(k,idt) =  con(k,idt-1)+xgap(j)
     der(k,idt) = dinta(k,con(k,idt))
     if(ityp(j).eq.5) go to 20
     x = (con(k,idt-1) + con(k,idt))/2.
     dint=dinta(k,x)
    15 phi(k,idt) =phi(k,idt-1) + xgap(j)*(der(k,idt-1) + der(k,idt) +
    &  4.*dint)/6.
     go to 25
    20 continue
     if (idt.eq.2) go to 35
     x=con(k,idt-1)-xgap(j)/5.
     dint=0.0
```

```
      do 23 n=1,6
      x = x + xgap(j)/5.
      23 dint=dint + dinta(k,x)*cons(n)
      phi(k,idt)=phi(k,idt-1)+dint*xgap(j)/288.
      go to 25
      35 pi=0.0
      xstr=0.0
      x=0.0
      xcheck=der(k,1)
      37 xcheck=xcheck/2.
      if(k.eq.2) go to 38
      xfin=(p(k,1)/xcheck)-(1.0/p(k,2))
      go to 39
      38 xfin=(p(k,1)/xcheck)-(1.0/p(k,2))
      39 if(xfin.gt.xgap(1)) go to 42
      xint=(xfin-xstr)/5.
      x=x-xint
      dint=0.0
      do 40 n=1,6
      x=x+xint
      40 dint=dint+dinta(k,x)*cons(n)
      pi=pi+dint*(xfin-xstr)/288.
      xstr=xfin
      go to 37
      42 xint=(xgap(1)-xstr)/5.
      x=x-xint
      dint=0.0
      do 45 n=1,6
      x=x+xint
      45 dint=dint+dinta(k,x)*cons(n)
      phi(k,2)=pi+dint*(xgap(1)-xstr)/288.
      25 continue
      go to 30
      write(67,2001)(con(k,i),i=1,110)
      write(67,2001)(phi(k,i),i=1,110)
      2001 format(10(2x,e11.4))
      30 continue
      return
      end
      subroutine datre(psin,ierr,iopt)
      implicit real*8(a-h,o-z)
       common phi(2,110),der(2,110),con(2,110),p(2,3),vint(2,3),cia(2),xk(2),cor
      if(iopt.eq.0) go to 30
      ierr=0
      do 20 j=1,2
      icheck=0
      5 icheck=icheck+1
      if(icheck.eq.110) go to 6
      if (phi(j,icheck).le.psin) go to 5
```

```
     & if (icheck.ge.110) ierr=1
     vint(j,1)=con(j,icheck-1)+(psin-phi(j,icheck-1))*
     &(con(j,icheck)-con(j,icheck-1))/(phi(j,icheck)-phi(j,icheck-1))
     vint(j,3)=(1./der(j,icheck)-1./der(j,icheck-1))/(phi(j,icheck)
     &-phi(j,icheck-1))
     xint=der(j,icheck-1)+(psin-phi(j,icheck-1))*(der(j,icheck)
     &-der(j,icheck-1))/(phi(j,icheck)-phi(j,icheck-1))
     20 vint(j,2)=1./xint
     return
     30 continue
     ierr=1
     psin=0.0
     do 40 j=1,2
      coint= cia(j)
     icheck=0
     35 icheck=icheck+1
     if(icheck.eq.111)return
     if(con(j,icheck).le.coint)go to 35
     if(phi(j,icheck).gt.psin)psin=phi(j,icheck)
     40 continue
     ierr=0
     return
     end
     function dinta(k,x)
     implicit real*8(a-h,o-z)
      common phi(2,110),der(2,110),con(2,110),p(2,3),vint(2,3),cia(2),xk(2),cor
     if(k.eq.2)go to 10
     dinta=(p(k,1)*p(k,2))/(1.0+(p(k,2)*x))
     return
     10 dinta=(p(k,1)*p(k,2))/(1.0+(p(k,2)*x))
     return
     end
```

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